885
7/21/65

UNCLASSIFIED
GEMP-47A

MASTER

Nuclear Materials & Propulsion Operation

HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 47, Part A

May 28, 1965

**PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.**

ADVANCED TECHNOLOGY SERVICES
GENERAL ELECTRIC

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, material, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, material, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission or his employment with such contractor.

Printed in USA. Price \$4.00. Available from the
Clearinghouse for Federal Scientific and
Technical Information,
National Bureau of Standards,
U. S. Department of Commerce,
5285 Port Royal Road,
Springfield, Virginia 22151

UNCLASSIFIED

GEMP-47A

UC-25 Metals, Ceramics,
and Materials
TID-4500 (41st Ed.)

**HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 47, Part A**

May 28, 1965

United States Atomic Energy Commission

Contract No. AT(40-1)-2847

**NUCLEAR MATERIALS and PROPULSION OPERATION
ADVANCED TECHNOLOGY SERVICES**

GENERAL ELECTRIC

Cincinnati 15, Ohio

UNCLASSIFIED

DISTRIBUTION

EXTERNAL

AEC Headquarters

G. K. Dicker W. R. Voight
F. C. Schwenk G. W. Wensch
J. M. Simmons M. J. Whitman

AEC, CANEL Project Office

A. J. Alexander

AEC, CAO

C. L. Karl
J. F. Weissenberg

AEC, OROO

D. F. Cope (3)
D. S. Zachry, Jr.

AEC, SAN

Col. J. B. Radcliffe, Jr.

Argonne National Laboratory

R. Noland

Atomics International

S. C. Carniglia
C. E. Weber

Battelle-Northwest

F. W. Albaugh J. J. Cadwell

BMI

S. Paprocki

Chase Brass & Copper

J. Port

General Atomic

D. Ragone

Institute for Defense Analyses

R. C. Hamilton

Jet Propulsion Laboratory

J. Davis

LASL

R. D. Baker

Lawrence Radiation Laboratory

C. Cline A. J. Rothman

NASA Headquarters

J. J. Lynch B. Reznick

NASA, Lewis Research Center

J. W. Creagh T. P. Moffitt N. D. Sanders
T. A. Moss L. Rosenblum N. Saunders
H. Schwartz

ORNL

R. E. Blanco P. Patriarca (2)
W. R. Grimes

Pratt and Whitney Aircraft (CANEL)

L. M. Raring (3)

Universal-Cyclops Steel Corporation

L. M. Bianchi

Westinghouse Astronuclear Lab.

D. C. Goldberg

Wah Chang Corporation

S. Worcester

INTERNAL

E. A. Aitken
W. G. Baxter
J. R. Beeler
J. C. Blake
B. Bonini
H. C. Brassfield
R. W. Brisken
V. P. Calkins
B. A. Chandler
C. L. Chase (3)
C. G. Collins
E. S. Collins
J. F. Collins
P. K. Conn
J. B. Conway

E. B. Delson
H. S. Edwards
E. W. Filer
P. N. Flagella
J. E. Fox
E. S. Funston
G. F. Hamby
J. O. Hibbits
A. N. Holden, APED (2)
L. D. Jordan
F. Kingsbury
G. Korton
W. C. Kuhlman
W. H. Long
J. E. McConnelee

L. R. McCreight, MSD
J. A. McGurty
C. I. McVey
J. W. Morfitt
J. Moteff
R. E. Motsinger
G. T. Muehlenkamp
C. E. Niemeyer
W. E. Niemuth
G. W. Pomeroy
W. Z. Prickett
R. Reid
F. C. Robertshaw
E. J. Schmidt, ATS
R. J. Spera

H. R. Stephan
C. L. Storrs
C. O. Tarr
P. P. Turner
F. O. Urban
G. R. VanHouten
H. Wagner
J. F. White
V. C. Wilson, RL
O. G. Woike
R. E. Wood
C. S. Wukusick
Library (10)

CONTENTS

	Page
1. Introduction and Summary	9
2. Oxidation-Resistant Fuel Element Materials Research (57001)	13
3. High-Temperature Reactor-Materials Research (57003)	27
4. Effect of Radiation on High-Temperature Metals and Alloys (57004)	85
5. High-Temperature Thermocouple and Electric Materials Research (57014) ...	101
6. Appendix	107

FIGURES

	Page
2.1 - Electron microprobe analysis for Fe, Cr, Al, and Y superimposed on photomicrographs of scanned areas of 2541-alloy-clad Fe - 50UO ₂ and (Fe - 25Cr) + 50UO ₂ specimens showing interdiffusion that occurred during 5000 hour tests at 1100°C in air	15
2.2 - Steps in fabricating 2541-clad Fe-UO ₂ specimen for in-pile test LTFC-1 ..	17
2.3 - Schematic drawing of in-pile test cartridge for LTFC series showing Fe-Cr-Al-Y-clad Fe-UO ₂ fuel element specimen double contained in stainless steel tubes and cooled by air flows up to 1700 liters per minute ..	19
2.4 - Hardness as a function of aging time at 425°C for irradiated 1541 alloy compared to unirradiated condition	21
2.5 - Hardness as a function of aging time at 450°C for 1541 alloy in irradiated and unirradiated condition	22
2.6 - Weight gain as a function of test time at 900°C and 1100°C in static air for Fe-Cr-Al-Y alloys for times up to 7000 hours	23
2.7 - Microstructure of surface oxides formed on 1041 alloy after 1800 hours at 550°C in steam	24
3.1 - Stress-rupture data for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen	29
3.2 - Linear creep rate data for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen	29
3.3 - Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen	30
3.4 - Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested at 2000°C in hydrogen	32
3.5 - Elongation at rupture versus temperature for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen	33
3.6 - Isochronal plot of stress-rupture data for arc-cast tungsten and molybdenum	33
3.7 - Larson-Miller parameter for arc-cast tungsten tested from 1600° to 3000°C	34
3.8 - Arc-cast tungsten specimens after creep-rupture testing at 2200°C and 2400°C	35
3.9 - Arc-cast tungsten specimens after creep-rupture testing at 2600°C and 2800°C	35
3.10 - Section of arc-cast tungsten after 237 hours at 2200°C and 0.70 kg/mm ² stress	36
3.11 - Section of arc-cast tungsten after 146 hours at 2400°C and 0.46 kg/mm ² stress	36

	Page
3.12 - Section of arc-cast tungsten after 0.78 hours at 2600°C and 0.84 kg/mm ² stress	36
3.13 - Section of arc-cast tungsten after 144 hours at 2800°C and 0.17 kg/mm ² stress	36
3.14 - Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested at 2400°C in hydrogen	37
3.15 - Creep curves for 0.115-cm-thick arc-cast tungsten sheet tested at 2400°C	37
3.16 - Creep curves for 0.15-cm-thick arc-cast tungsten at 2600°C	39
3.17 - Creep curves for 0.15-cm-thick arc-cast tungsten at 2800°C	39
3.18 - Creep curve ($\epsilon - \epsilon_0$) for 0.15-cm-thick arc-cast tungsten sheet tested at 2400°C, showing linearity during first stage of creep	40
3.19 - Strain versus $t^{0.6}$ for 0.15-cm-thick arc-cast tungsten sheet at 2400°C, showing linearity during first stage of creep	41
3.20 - Plot of "b" versus stress showing constant slope "c" for arc-cast tungsten from 2200°C to 2800°C	43
3.21 - Plot of "a" versus temperature showing linearity for arc-cast tungsten from 2200°C to 2800°C	44
3.22 - Analysis of the equation, $\epsilon = f + gt - he^{-Pt}$, for arc-cast tungsten data at 2400°C and 0.84 kg/mm ²	45
3.23 - Experimental first-stage creep data for 0.15-cm-thick arc-cast tungsten sheet at 2400°C shown in comparison to curves calculated using constants in Table 3.3	48
3.24 - Creep-rupture specimens of arc-cast molybdenum rods (0.4 cm in diameter) after testing at 2200°C in hydrogen	49
3.25 - Arc-cast molybdenum rod after annealing at 2200°C for 2 hours in hydrogen	50
3.26 - Photomicrograph and Laue pattern for the same transverse section of an arc-cast molybdenum rod after 2.66 hours (rupture) at 2200°C and 0.32 kg/mm ² stress	51
3.27 - Photomicrograph and Laue pattern for the same transverse section of an arc-cast molybdenum rod after 17 hours (rupture) at 2200°C and 0.20 kg/mm ² stress	52
3.28 - Photomicrograph and Laue pattern for the same transverse section of an arc-cast molybdenum rod after 145.2 hours (rupture) at 2200°C and 0.14 kg/mm ² stress	53
3.29 - Laue pattern from longitudinal section of an arc-cast molybdenum rod after rupture at 2200°C and 0.32 kg/mm ² stress	54
3.30 - Longitudinal section of arc-cast molybdenum rod after rupture at 2200°C and 0.20 kg/mm ² stress	55
3.31 - Diagonal section of arc-cast molybdenum rod after rupture at 2200°C and 0.32 kg/mm ² stress	55
3.32 - Diagonal sections of arc-cast molybdenum rods cut along slip planes after rupture at 2200°C in hydrogen	57
3.33 - Schematic of electro-optical extensometer tracker (Optron)	58
3.34 - Optron and furnace for creep testing to 3000°C	59
3.35 - Electron-beam-welded tungsten wire targets used for the measurement of creep with the Optron	59
3.36 - Creep curve for arc-cast molybdenum (Specimen M-6-44) at 2200°C and 0.30 kg/mm ² stress in helium	62
3.37 - Creep curve for arc-cast molybdenum (Specimen M6-2-4) at 1800°C and 1.20 kg/mm ² stress in helium	62

	Page
3.38 - Strain versus $t^{0.7}$ for arc-cast molybdenum at 1800°C and 1.20 kg/mm ² stress	63
3.39 - Results of ultrasonic and X-ray inspection of W - 25Re sheet, EV-1	66
3.40 - Results of ultrasonic and X-ray inspection of W - 25Re sheet, EV-2	67
3.41 - Results of ultrasonic and X-ray inspection of W - 25Re sheet, EV-3	68
3.42 - Results of ultrasonic and X-ray inspection of W - 25Re sheet, EV-4	69
3.43 - Results of ultrasonic and X-ray inspection of W - 25Re sheet, EV-5	70
3.44 - Results of ultrasonic and X-ray inspection of W - 25Re sheet, EV-7	71
3.45 - Commercial W - 25Re as-received and after room-temperature bend test following a 30-minute treatment in H ₂ at 3000°C	74
3.46 - W - 25Re specimen EV-7 after 30-minute treatment in H ₂ at 3000°C	76
3.47 - Creep curves for W-Re alloys at 1600°C and 4.22 kg/mm ² in hydrogen	79
3.48 - Creep curves for W - Re - 10Mo alloys at 1600°C and 4.22 kg/mm ² in hydrogen	80
3.49 - Creep curves for W - Re - 20Mo alloys at 1600°C and 4.22 kg/mm ² in hydrogen	80
3.50 - Chromium-base alloys after 50 percent reduction by cold-pressing.....	83
4.1 - Comparison of strain measured across the center 2.54 cm of gage section determined by the twin-scope optical extensometer with the apparent strain across the total gage section (4.45 cm) determined from the total load-train movement	90
4.2 - Temperature-compensated time correction factor as a function of time for several assumed activation energies for defect migration	91
4.3 - Isothermal resistivity recovery of recrystallized tungsten irradiated in ORM-14 at 779.5°, 820°, and 858°C	92
4.4 - Isothermal resistivity recovery of recrystallized tungsten irradiated in ORM-11 at 779.5°, 820°, and 858°C	92
4.5 - Resistivity of as-received (stress-relieved) tungsten wire	93
4.6 - Hardness of irradiated and unirradiated polycrystalline molybdenum as a function of temperature	94
4.7 - Room-temperature hardness of irradiated polycrystalline molybdenum as a function of temperature	95
4.8 - Room-temperature yield stress and hardness of irradiated molybdenum as a function of the annealing homologous temperature	96
4.9 - Stress-rupture properties of Hastelloy N at 816°C.....	97
4.10 - Strain versus time for Hastelloy N specimens tested in air at a temperature of 650°C and a stress of 24.6 kg/mm ²	98
5.1 - Comparison of thermoelectric output as a function of temperature for various metals and alloys versus W - 25Re commercial wire	102
5.2 - Resistivity of ThO ₂ and BeO as a function of temperature and oxygen partial pressure	104
5.3 - Photograph showing the microstructure of a Nb-to-Lucalox graded seal bonded at 700 kg/cm ² , 1650°C, 1 hour	105
5.4 - Photograph showing the microstructure of a thin BeO layer between two Nb sheets, forming an electrically insulated but high thermal conductivity metal-to-ceramic seal	106

TABLES

	Page
2.1 - Summary of Fe-Cr-Al-Y-clad fueled specimens undergoing thermal stability tests in air	14
2.2 - Compositions of alloys with low yttrium contents added to impact studies ..	20
2.3 - Approximate ductile-to-brittle transition temperatures for bend and impact tests	20
2.4 - Weight gain data for pre-oxidized Fe-Cr-Al-Y alloys tested in steam at 550°C and 730°C for 4000 hours	25
2.5 - Weight gain data for alloys tested at 730°C in steam	26
3.1 - Creep-rupture results for arc-cast tungsten from 1600°C to 3000°C in hydrogen	28
3.2 - Illustration of de Lacombe calculation procedure based on finite differences	42
3.3 - Constants for use in various creep equation forms for arc-cast tungsten ..	47
3.4 - Creep data for arc-cast molybdenum at 1800°C and 2200°C obtained with the Optron	60
3.5 - Chemical composition of six lots of purchased W - 25Re sheet	64
3.6 - Voids detected radiographically in simulated electron-beam welds on W - 25Re sheet	65
3.7 - Summary of non-destructive tests on commercial W - 25Re	72
3.8 - Room-temperature bend tests for commercial W - 25Re sheet following prolonged holding at high temperatures	73
3.9 - Ductility versus temperature of commercial W - 25Re as determined by bend tests	76
3.10 - Chemical analyses of powder metallurgy W-Re-Mo alloys after fabrication into 0.05 cm sheet	78
3.11 - Creep-rupture results for W-Re-Mo alloys at 1600°C and 4.22 kg/mm ² stress in hydrogen	79
3.12 - Room-temperature bend test results for alloys held in hydrogen for 10 or 100 hours at the indicated temperature	81
3.13 - Sigma phase precipitation in W-Re and W-Re-Mo alloys as influenced by high temperatures	82
3.14 - Compositions, ductility rating, and average electron-to-atom ratio of chromium alloys	84
4.1 - Summary of major experiments in the refractory metals and alloys radiation effects program	86
4.2 - Irradiation data for refractory-metal capsules	88

CONVERSION TABLE

To Convert From	To	Multiply By
Atmospheres	Pounds/inch ²	14.7
Calories (mean)	Btu (mean)	0.00397
Calories/gram-°C	Btu/pound-°F	1.0
Calories/sec-cm-°C	Btu/hr-ft-°F	241.8
Calories/sec-cm ²	Btu/hr-ft ²	1.32 x 10 ⁴
Calories/sec-cm ² -°C	Btu/hr-ft ² -°F	7370
Centimeters	Feet	0.03281
	Inches	0.3937
Cubic centimeters	Cubic feet	3.531 x 10 ⁻⁵
	Cubic inches	0.06103
Grams	Pounds	0.002205
Grams/cm ³	Pounds/ft ³	62.43
Grams/cm ²	psi	0.01422
Kilograms	Pounds	2.205
Kilograms/cm ²	Atmospheres	0.9678
	Pounds/ft ²	2048
	Pounds/inch ²	14.22
Kilograms/mm ²	Pounds/inch ²	1422.32
Kilowatts	Btu/sec	0.948
Liters	Cubic feet	0.0353
Meters	Inches	39.37
Millimeters of mercury	Atmospheres	0.001316
Square centimeters	Square feet	0.001076
	Square inches	0.155
Torr	mm of Hg	1.0
	Atmospheres	0.001316
Watts/cm-°C	Btu/hr-ft-°F	57.8
Watt-seconds	Btu	0.000948
Watts/cm ² -°C	Btu/hr-ft ²	3170
Watts/cm ² -°C	Btu/hr-ft ² -°F	1760
Centimeters/sec	Feet/sec	0.03281
Meters/sec	Feet/sec	3.281

1. INTRODUCTION AND SUMMARY

Introduction

This report is the unclassified portion of the forty-seventh in a series of monthly reports of the work in process on materials development for the Atomic Energy Commission under Contract AT(40-1)-2847.

Included is a summary of the work from February 1, 1965 to April 15, 1965, on four of the fourteen specific development programs in process. Two of the remaining programs are reported in the classified portion of this report, GEMP-47, Part B. The other eight programs, involving the development of ceramic fuel materials, are reported in alternate months.

Summary

OXIDATION-RESISTANT FUEL ELEMENT MATERIALS RESEARCH (57001)

Laboratory testing of Fe-Cr-Al-Y-clad fueled specimens has exceeded 6700 hours at 1100°C and 950°C in air with continuing indication of excellent stability. The presence of uranium at low concentration was detected by electron microprobe analysis in the 2541 alloy cladding of an Fe-Cr-UO₂ specimen after 5000 hours at 1100°C. No uranium diffusion was detected for a 2541-clad Fe-UO₂ core tested under the same conditions.

An in-pile test, LTFC-1, of a 2541-clad Fe - 40UO₂ specimen is operating in the LITR at 1100°C maximum specimen temperature. A prototype specimen of in-pile design tested in the laboratory for 2600 hours at 1100°C shows no visible change.

Apparently, irradiation of aged 1541 alloy causes partial solutioning of the precipitate as indicated by post-irradiation aging at 425°C. Oxidation resistance of the irradiated alloy at 900°C was the same as for unirradiated material after 200 hours.

Corrosion testing of various compositions of Fe-Cr-Al-Y alloys has continued in both air and superheated steam at temperatures of 450° to 1100°C for times up to 7000 hours. The Fe-Cr-Al-Y alloys continue to exhibit lower weight gains in steam at 730°C than nickel-base alloys or ferritic stainless steels.

HIGH-TEMPERATURE REACTOR MATERIALS RESEARCH (57003)

Creep-rupture tests of arc-cast tungsten were completed at several stress levels at temperatures of 1600°, 2000°, 2200°, 2400°, 2600°, and 2800°C; in addition, a test of this material at a stress of 0.21 kg/mm² at 3000°C was successfully completed, repre-

senting the highest test temperature ever recorded for a creep-rupture evaluation of any material. Values of the time required to obtain certain percent elongations are presented for arc-cast tungsten with stress-rupture and second-stage creep behavior correlated in the usual manner. Particular emphasis in these tests was given to an analysis of first-stage creep behavior; a parabolic creep law with an exponent of 0.6 seems to be followed fairly exactly at all temperatures evaluated to date.

Arc-cast molybdenum rod, creep-rupture-tested at 2200°C, was analyzed by X-ray diffraction and optical microscopy. Both techniques showed a high degree of polygonization for the high-stress, short-time-to-rupture specimens, with a decrease occurring in the amount of polygonization as the stress was decreased. Back-reflection photographs of longitudinal sections reveal that the orientation was primarily [001] with a strong <110> directionality along the axis of applied stress.

An electro-optical extensometer (Optron)* was evaluated for the purpose of measuring creep automatically at elevated temperatures. Excellent agreement was noted for arc-cast molybdenum using the Optron at temperatures of 1800°C and 2200°C when the results were compared to data previously obtained for the same material and tested at the same conditions. First-stage creep data for arc-cast molybdenum, obtained with the Optron, were analyzed on the basis of the conventional parabolic creep law, $\epsilon = bt^m + \epsilon_0$. Values of b , ϵ_0 , and m (constants) were determined for all the tests performed to date with the value for the exponent, m , approximating 0.65.

The quality and apparent reliability of W - 25Re sheet purchased from commercial vendors was generally unsatisfactory for advanced reactor applications. A major defect observed in the sheet was edge laminations believed attributable to trimming operations. Large areas of the sheet were rejected due to internal defects detected by ultrasonic testing. Very poor surface texture and thickness control were observed for much of six lots of material evaluated. Room-temperature bend tests conducted after holding test pieces at temperatures up to 3000°C (in H₂) showed the powder-metallurgy sheet to be generally more ductile than arc-cast process sheet.

Creep-rupture tests of twelve W-Re-Mo alloys were performed at 1600°C and a stress of 4.22 kg/mm² to evaluate the effect of varying the rhenium content from 26 to 29 percent and the molybdenum content from 0 to 20 percent. The W - 26Re alloy had the longest rupture life and was the most creep-resistant. Specimens of W - 28Re and W - 29Re, some of which contained 10 percent molybdenum, showed a significant first-stage creep whereas all other specimens showed little or no first-stage creep.

The same twelve W-Re-Mo alloys mentioned above were given room-temperature bend ductility tests after holding for periods to 100 hours in the 1200°C to 2600°C range. After holding at 2600°C, the ternary W-Re-Mo alloys developed more bend ductility than binary W-Re alloys. As anticipated, bend ductility and hardness values throughout the series were basically a function of rhenium content with molybdenum acting to lower hardness and increase ductility.

Ruthenium was shown to increase the ductility of chromium with the reaction proportional to the electron-to-atom ratio of the alloy. Rhenium has a lower ductilizing effect than ruthenium as a chromium addition on an atom-to-atom basis. Molybdenum added to chromium with ruthenium present as a ductilizing addition had no readily observable influence on ductility of the ternary alloy.

*Registered trade name of Optron Corporation, Santa Barbara, California.

EFFECT OF RADIATION ON HIGH-TEMPERATURE METALS AND ALLOYS (57004)

Optical extensometer measurements across a central portion of tungsten specimen gage sections indicate that the creep rates are approximately 13 percent greater than the strain rates determined across the complete gage length obtained by observing total load train movement. This difference is attributed to the slightly larger temperature profile occurring across the central portion of the specimen. The difference should be the same for both irradiated and control specimens and will not significantly alter the magnitude of the radiation-induced changes observed to occur.

Resistivity recovery studies of tungsten in the temperature region of $0.31 T_m$ were made on specimens irradiated at two different dosages (1.3 and 3.3×10^{-19} nvt, $E_n \geq 1$ Mev). Annealing one of the high dose specimens at a temperature of 850°C for times up to 100 hours shows that the defect density is still changing and that saturation recovery, therefore, has not yet been reached. Data reduction and analysis were initiated on this phase of the annealing studies.

Hot-hardness measurements of irradiated molybdenum show results similar to those obtained for the case of irradiated tungsten specimens. A peak in the irradiation-induced hardness value appears at a temperature of approximately 160°C . In addition, the room temperature hardness values following annealing at a higher temperature show an increase in the radiation-induced hardening over and above that observed for the as-irradiated condition. These results (i. e., the further hardening) reflect similar trends observed in the room temperature yield properties of several BCC metals following irradiation. Recovery is observed to begin at a temperature of approximately 700°C and is apparently completed at a temperature of about 900°C .

Preliminary studies on the effects of neutron irradiation on Hastelloy N specimens irradiated to a fast neutron dose of approximately 1×10^{20} nvt show about a factor of 10 reduction in the time to rupture when tested at a temperature of about 650°C . This material shows similar elevated temperature embrittlement to that observed in the Hastelloy X alloys when irradiated to comparable neutron dosages.

HIGH-TEMPERATURE THERMOCOUPLE AND ELECTRICAL MATERIALS RESEARCH (57014)

The thermoelectric potentials to 1800°C of 12 materials with low neutron-capture cross sections indicate Mo, Mo - 1Ru, and Mo - 1 Os (at. %) versus Nb have merit as thermocouples to 1200°C and possibly higher by modifying the Nb.

The electrical resistivity of ThO_2 and BeO is influenced by oxygen partial pressure at temperatures above 1400°C .

A Nb-to-Lucalox graded seal withstood 100 thermal cycles between 650°C and 1450°C at heating and cooling rates of 300°C per minute.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

2. OXIDATION-RESISTANT FUEL ELEMENT MATERIALS RESEARCH

(57001)

The objective of this program is to develop fuel element materials for use at high temperatures in air, steam, or oxidizing coolants which are superior to presently available fuel materials in terms of high-temperature capabilities, long-time service life, and containment of fission products.

FUEL ELEMENT MATERIALS EVALUATIONS

Previous studies have shown that the Fe-Cr-Al-Y family of alloys is more resistant to high-temperature air or steam corrosion than any known commercial alloy that may be suitable for fuel element cladding. These alloys have been proven to be reliable as cladding over Fe-UO₂ and Cr-UO₂ cores in laboratory tests for at least 5000 hours at 1100°C in air and are continuing on test toward a goal of 10,000 hours. An in-pile test of a 2541-alloy-clad¹ Fe - 40UO₂² specimen was started in the LTR at 1100°C in flowing air to determine the fission product retention capability of the cladding.

Fueled Capsule Test Program

Long-time laboratory test data on the clad fuel element systems with the most promising high-temperature capabilities are being obtained from capsule specimens,³ 1.05 cm in diameter by 2.54 cm in length, clad with 0.50-mm-thick 1541 or 2541 alloy, and auto-clave bonded. The goal of the capsule specimen test program is 10,000 hours at 950°C and 1100°C in flowing air. Specimens are periodically analyzed by nondestructive X-ray fluorescence methods for uranium diffusion to the surface of the cladding. A specimen from each group is removed from test for destructive analysis after completion of scheduled test periods of 1000, 3000, 5000, and 7500 hours.

A total of 45 specimens was on test at the close of this report period. The status of current test specimens is summarized in Table 2.1. With few exceptions, the specimens with UO₂ cores containing agglomerated fuel particles and clad with either 2541 or 1541 alloy continue to show excellent oxidation resistance at 950°C and 1100°C for times in excess of 5500 hours. Specimens containing plasma-arc spheroidized UO₂ particles, recently added to the test group, have accumulated about 2000 hours of test time at 950°C and 1100°C with no apparent detrimental effects. Specimens containing Cr-UO₂ cores continue to show stability comparable to those containing Fe-UO₂ cores, based on X-ray fluorescence analyses for uranium diffusion and metallographic examination.

Metallographic analyses, including electron microprobe scanning, were completed on two of the six capsule specimens removed from the test after completing 5000 hours at 1100°C (Figure 2.1). Both specimens were clad with 2541 alloy and the cores contained

¹2541 alloy composition is Fe - 25Cr - 4Al - 1Y; 1541 alloy composition is Fe - 15Cr - 4Al - 1Y.

²Cladding alloy compositions are given in weight percent and core compositions in volume percent.

³"Third Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-270B, February 28, 1964, p. 103.

TABLE 2.1
SUMMARY OF Fe-Cr-Al-Y-CLAD FUELED SPECIMENS
UNDERGOING THERMAL STABILITY TESTS IN AIR

Cladding	Core Composition, vol %	Type Fuel ^a	Specimen Number	Test Temperature, °C	Current Test Time, hr	Relative Diffusion Of Uranium ^b	Status ^c
2541	Fe - 50UO ₂	KM-A	FAU-17	950	5610	ND	Terminated
			FAU-36	950	5610	ND	
			FAU-38	950	5610	ND	
			FAU-15	1100	5015	ND	
			FAU-16	1100	5825	ND	
			FAU-37	1100	4670	ND	
1541	Fe - 50UO ₂	KM-A	FAU-18	1100	4670	<1	
2541	Fe - 40UO ₂	AR	FU-29	950	5610	ND	
			FU-30	1100	4670	1	
			FU-32	1100	4440	ND	
2541	Fe - 40UO ₂	GE-A	FAU-45	1100	2045	<1	
			FAU-46	1100	2045	ND	
2541	Fe - 40UO ₂	KM-A	FAU-19	950	2045	1.5	Terminated
			FAU-21	950	2045	ND	
			FAU-27	950	2725	<1	
			FAU-28	950	2725	ND	
			FAU-20	1100	3025	ND	
			FAU-22	1100	4440	<1	
			FAU-25	1100	2675	<1	
			FAU-30	1100	2045	ND	
			FAU-49	1100	2045	ND	
2541	Fe - 40UO ₂	S-KM	FSU-9	950	1975	<1	
			FSU-13	950	1975	ND	
			FSU-10	1100	1975	<1	
			FSU-11	1100	1975	<1	
			FSU-12	1100	1975	<1	
1541	Fe - 40UO ₂	S-KM	FSU-19	950	1975	ND	
			FSU-20	950	1975	ND	
			FSU-21	950	1975	ND	
			FSU-15	1100	1975	2	
			FSU-16	1100	1975	2	
			FSU-17	1100	1975	1.5	
2541	Fe - 25UO ₂	AR	FU-52	1100	4670	ND	
2541	Fe - 25UO ₂	KM-A	FAU-33	1100	<3505	-	Ruptured
2541	Cr - 50UO ₂	AR	CU-26	950	6470	<1	
			CU-25	1100	4670	1.5	
2541	Cr - 50UO ₂	KM-A	CAU-27	1100	3600	2	
			CAU-28	1100	4670	1	
1541	Cr - 50UO ₂	KM-A	CAU-26	950	5110	ND	Terminated
1541	Cr - 50(UO ₂ - 11ThO ₂)	GE-A	CUT-23	950	6610	ND	
			CUT-24	1100	3600	1	
2541	(Fe - 25Cr) - 50UO ₂	AR	FCU-3	950	5070	ND	Terminated
2541	(Fe - 25Cr) - 50UO ₂	KM-A	FCAU-4	950	6470	ND	Terminated
			FCAU-2	1100	5015	50	
			FCAU-3	1100	5765	<1	
1541	Fe - 40UN	AR	FUN-8	950	5610	ND	
2541	Cr - 40UN	AR	CUN-5	950	7110	1	Terminated
			CUN-4	1100	5010	25	
1541	Cr - 50UN	AR	CUN-7	1100	4670	27	
2541	(Fe - 25Cr) - 40UN	AR	FCUN-1	950	7110	<1	Terminated
			FCUN-2	1100	5015	<1	
			FCUN-3	1100	3600	9	
1541	(Fe - 25Cr) - 40UN		FCUN-5	950	5610	ND	

^aAR - Ceramic-grade UO₂ or UN of -325 mesh particle size.

GE-A - UO₂ agglomerated at GE-NMPO, -100/+200 mesh.

KM-A - Commercial agglomerated UO₂, -100/+200 mesh.

S-KM - UO₂ plasma spheroidized at GE-NMPO, -140/+200 mesh.

^bAnalysis of cladding surface for uranium by X-ray fluorescence relative to an arbitrary standard specimen. ND indicates uranium not detected within limits of method (~500 ppm).

^cUnless otherwise noted, specimens are continuing on test satisfactorily.

Fe-50UO₂
Specimen No. FAU-15 (Neg. 5349)

(Fe-25Cr) + 50UO₂
Specimen No. FCAU-2 (Neg. 5351)

Fig. 2.1 - Electron microprobe analysis for Fe, Cr, Al, and Y superimposed on photomicrographs of scanned areas of 2541-alloy-clad Fe-50UO₂ and (Fe-25Cr) + 50UO₂ specimens showing interdiffusion that occurred during 5000 hour tests at 1100°C in air (100X)

50 volume percent commercial agglomerated UO_2 . The core matrix of specimen FAU-15 was Fe and that of specimen FCAU-2 was Fe - 25Cr. Both specimens showed good fuel distributions with clean, high-density matrices; however, some porosity and fracturing of the fuel particles was evident. Specimen FAU-15, containing an Fe - 50 UO_2 core, had a continuous alumina barrier between the 2541 alloy cladding and the core. The voids in the cladding near the interface were caused by pull-out of brittle intergranular (Y_2O_3) material. A small amount of intergranular Y_2O_3 was also present near the surface of the cladding. A thin, protective oxide layer covered the surface of the cladding. The microprobe analyses show the interdiffusion of chromium into the core and iron into the cladding and increased concentrations of aluminum and yttrium near the interface. The yttrium peak which occurred near the surface of the cladding was probably caused by Y_2O_3 particles. No uranium was detected in the cladding.

Specimen FCAU-2, containing an (Fe - 25Cr) - 50 UO_2 core, did not exhibit a continuous alumina barrier at the interface; however, a discontinuous, thin alumina layer occurred on the side toward the cladding of some of the fuel particles near the interface. Some of the fuel particles also contained a fine metallic phase near their outer surfaces. The amount of intergranular Y_2O_3 in the cladding was somewhat greater than for specimen FAU-15. This specimen showed no changes in iron and chromium concentrations between the core and cladding. Peaks in aluminum and yttrium concentration occurred in the area of the interface and some diffusion of aluminum into the core was indicated. This explains the alumina layers observed on fuel particles in the core for a distance of about 100 microns. The presence of uranium ($> 500 \text{ ppm}^4$) was detected in the cladding but at very low concentration. X-ray fluorescence analyses performed on the surface of this specimen periodically up to 4800 hours indicated relative uranium concentrations of less than one until the last measurement was made after 5000 hours, when an increase to 50 on a relative scale was noted. This is a good confirmation of the X-ray fluorescence analysis for uranium penetration and its correspondence with the electron microprobe scanning technique for diffusion.

A more sensitive method of detecting uranium diffusion is analysis for alpha activity on the cladding surface of specimens containing enriched UO_2 in the core. A series of specimens containing enriched UO_2 , Fe - 40 UO_2 , and (Fe - 25Cr) - 40 UO_2 is being prepared to obtain confirming information on the compatibility of UO_2 and Fe-Cr-Al-Y cladding alloys. These specimens will be analyzed by the alpha counting technique and compared with X-ray fluorescence analyses and electron microprobe scans. Testing of enriched fuel specimens will be performed at the current test temperatures of 950°C and 1100°C, and also at 730°C to obtain data of interest for superheat steam reactors.

In-Pile Testing

A series of in-pile tests of the Fe-Cr-Al-Y clad fuel elements is planned to demonstrate fission product retention capabilities as a function of temperature and burnup capabilities at various temperatures. These irradiation tests will be conducted at the Oak Ridge National Laboratory using both the LITR and the ORR.

LTFC-1 - The first in-pile test in this series, LTFC-1, is currently operating in the C-48 facility of the LITR. The fuel element specimen in this test is of a tubular design having the thin fueled core section necessary to achieve uniform fuel burnup (Figure 2.2).

Six specimens containing Fe - 40 UO_2 cores (agglomerated UO_2 of 70% enrichment) and clad with 0.76-mm-thick 2541 alloy were fabricated for this in-pile test and for supporting laboratory tests. The core compacts were sintered at 1200°C in hydrogen and then processed in the autoclave to obtain high density before machining. This resulted in compacts of above 98 percent of theoretical density. The assembled specimen was TIG-welded at

⁴Sensitivity of electron microprobe for detecting uranium.

GE-NMPO

Enriched Fe-40UO₂ fuel core and 2541 alloy cladding components
ready for assembly (Neg. P64-7-32C)

GE-NMPO

After gas pressure bonding and machining to final size (Neg. P65-3-18)

Fig. 2.2—Steps in fabricating 2541-clad Fe-UO₂ specimen for in-pile test
LTFC-1

each end using a small ring insert of Fe - 25Cr to dilute the yttrium content of the weld and avoid possible porosity. Final seal was made by electron-beam welding after evacuation of the core through a small vent hole. All components were gas pressure bonded in the autoclave at 1250°C and then the specimens were machined to final shape as shown in Figure 2.2.

One of the six specimens fabricated was not leak-tight, but the other five passed the rigid inspection for quality that is required for in-pile testing. The specimen chosen for test LTFC-1, designated as CFEAU-2, contains 5.5 grams of U²³⁵ in an Fe - 40UO₂ core weighing 18.6 grams.

The in-pile test cartridge design provides double containment of the specimen in a stainless steel capsule as shown in Figure 2.3. The test condition requires air coolant flow of 1700 liters per minute over the outside surface of the fuel element specimen to hold the temperature to 1100°C maximum in a thermal neutron flux of 5×10^{12} nv. Under these conditions, the heat extraction rate will be 1 Btu per second. The specimen is instrumented with five thermocouples (Pt / Pt - Rh) all located inside a solid core plug in the center tube.

Test LTFC-1 is planned to operate at a specimen temperature of 1100°C for 1000 hours, equivalent to about seven weeks in the LITR. Sampling of the exit air for fractional release of fission gases, using charcoal traps, will be performed periodically.

The cartridge was initially positioned 15 cm from peak flux so a lower flow of coolant air could be maintained while establishing fission product sampling procedures to be used at high flow rates. A charcoal trap sampling taken after 76 hours at 1100°C in this initial position indicated a fractional release of Xe¹³⁵ of 3×10^{-7} , which is higher than expected normally from recoil release.

In-pile specimens with 1541 alloy cladding and Fe-UO₂ enriched cores have also been fabricated and one of these will be used in the assembly of the next test cartridge, LTFC-2, which is scheduled for testing in the LITR early in the next fiscal year.

Laboratory Testing - Prototype specimens of the in-pile test design containing depleted UO₂ and clad with 2541 and 1541 alloy have been tested in the laboratory at 1100°C for times up to 2600 hours with no visible changes. Specimens with 1541 alloy cladding appear as oxidation resistant after 1500 hours at 1100°C as those with 2541 alloy cladding.

A specimen containing enriched UO₂ has passed 470 hours at 1100°C with periodic monitoring of the cladding surface by alpha counting. At 420 hours the average alpha count was about 425 counts per minute over the fueled area (8.35 cm²) indicating gradual diffusion of uranium through the 0.76-cm-thick cladding.

IRON-BASE ALLOY DEVELOPMENT

The objective of this portion of the work is to improve the structural properties of the Fe-Cr-Al-Y alloys without sacrificing oxidation or corrosion resistance.

Property Measurements

An impact test, described previously,⁵ is being used to compare alloy compositions and effects of heat treatments. Standard V-notch Charpy tests are being performed at the Naval Research Laboratory on the 1541 alloy and similar tests will be performed on optimum alloys at GE-NMPO.

It was previously determined⁶ that the ductile-to-brittle transition temperature (DBTT) of an Fe-Cr-Al-Y alloy containing nominal 1 percent yttrium is about 125°C compared

⁵"High-Temperature Materials Program Progress Report No. 41, Part A," GE-NMPO, GEMP-41A, November 30, 1964, p. 17.

⁶"High-Temperature Materials Program Progress Report No. 43, Part A," GE-NMPO, GEMP-43A, January 29, 1965, p. 17.

Fig. 2.3 - Schematic drawing of in-pile test cartridge for LTFC series showing Fe-Cr-Al-Y-clad Fe-UO₂ fuel element specimen double contained in stainless steel tubes and cooled by air flows up to 1700 liters per minute (Dwg. 219R376 Ref.)

to -25°C for a non-yttrium-containing alloy. During this report period, low yttrium alloys were added to the impact studies, Table 2.2. Impact tests indicate that the toughness (absorbed energy) is increased above the DBTT by a factor of about two as the yttrium is reduced from 1.0 to 0.35 percent, but the DBTT remains about the same as for the high yttrium alloys. Since the yttrium is present as particles of YFe_2 , it is believed that the particles in some manner control the DBTT.

TABLE 2.2
COMPOSITIONS OF ALLOYS WITH LOW YTTRIUM CONTENTS
ADDED TO IMPACT STUDIES

Heat No.		Composition								
		Wt % ^a			ppm					
		Cr	Y	Al	C	S	Si	O ₂	N ₂	H ₂
MS-10	Nominal	25	0.5	3						
	Analysis	24.7	0.18	2.92	30	20	100	50	1	2
MS-11	Nominal	25	0.75	4						
	Analysis	24.7	-	4.08	440	30	100	44	7	2
MS-13	Nominal	25	0.35	4						
	Analysis	24.3	0.12	3.98	160	20	-	13	7	1

^aRemainder iron.

Specimens of several alloys were aged at 450°C for 1000 hours in evacuated quartz capsules. The changes in the DBTT for both impact and bend tests are presented in Table 2.3. In both the bend and impact tests, aging at 450°C increased the DBTT about 200°C for the 2541 alloy and about 100°C for the 1541 alloy. The addition of 5 percent molybdenum to the 1541 alloy increased the DBTT to a level comparable to the aged 2541 alloy. The 450°C embrittlement in the 1341, 1041, and 0561⁷ alloys should be progressively less. Impact tests on these alloys are in progress. The changes in DBTT for these various alloys correlate well with hardness changes obtained during aging at 450°C .

TABLE 2.3
APPROXIMATE DUCTILE-TO-BRITTLE TRANSITION TEMPERATURES
FOR BEND AND IMPACT TESTS

Alloy	Hardness, R _A		Ductile-To-Brittle Transition Temperature, $^{\circ}\text{C}$			
			Bend Tests ^b		Impact Tests	
	As-Annealed	Aged ^a	As-Annealed	Aged ^a	As-Annealed	Aged ^a
2541	56	68.0	<-80	~120	~150	300 - 350
1541	51.8	61.0	<-80	~30	~180	200 - 250
1541 + 5Mo	56.7	66.4	c	>25	-	250 - 350
1341	54.0	55.5	c	c	-	-
1041	48.0	51.0	c	c	~160	-
0561	51.8	51.8	c	c	150 - 200	-

^aAged for 1000 hours at 450°C .

^bSheet specimen 0.76 mm thick, bend radius - 1.5 mm.

^cDBTT not determined, 90-degree bend at room temperature.

Irradiation Effects

The effects of irradiation on the properties of the Fe-Cr-Al-Y alloys are being studied. Initially, bend specimens of 1541 alloy (Heat MS-38) were irradiated to 3×10^{19} nvt in the

⁷1341 alloy composition is Fe-13Cr-4Al-1Y; 1041 is Fe-10Cr-4Al-1Y; and 0561 is Fe-5Cr-6Al-1Y.

ORR at pile ambient temperature. Hardness data presented previously⁸ demonstrated that irradiation caused either overaging or solutioning of the precipitate in an aged alloy, and that the effects of irradiation were removed by annealing for 1 hour at 300° to 350°C.

Irradiated specimens of 1541 alloy were aged at 300°C and 425°C for 2252 hours, at 350°C for 1200 hours, and at 450°C for 1000 hours. In specimens aged at 300°C and 350°C, after an initial drop in hardness corresponding to the annealing out of irradiation effects, no age-hardening occurred. The specimens aged at 425°C showed an initial hardness decrease followed by an increase in hardness as shown in Figure 2.4. The aged plus irradiated specimens gradually attained a hardness level equal to that of the unirradiated specimens. These data, while not conclusive, indicate that the irradiation caused partial solutioning of the precipitate. If overaging had occurred, the hardness of the aged plus irradiated specimen would probably have remained below that of the unirradiated specimen. The difference in hardnesses of the annealed and the annealed plus irradiated specimens is not understood. The difference was not noted in specimens aged at 450°C as shown in Figure 2.5.

Fig. 2.4—Hardness as a function of aging time at 425°C for irradiated 1541 alloy compared to unirradiated condition

Both irradiated and control specimens were oxidized at 900°C in a muffle furnace in static air. The specimens were removed periodically and weighed. In all cases the weight gains were low, less than 1 mg/cm², and indicated no significant differences in oxidation rate after 200 hours.

Another series of 72 bend test specimens, consisting of 2541, 1541, 1041, and 0561 alloys, has been irradiated for 535 hours at ambient temperature to 0.925×10^{20} nvt (fast flux) in the ETR (GEFP2-220). The specimens are awaiting evaluation.

⁸“High-Temperature Materials Program Progress Report No. 43, Part A,” GE-NMPO, GEMP-43A, January 29, 1965, p. 20.

Fig. 2.5 – Hardness as a function of aging time at 450°C for 1541 alloy in irradiated and unirradiated condition

Air-Oxidation Studies

Air-oxidation tests of a series of Fe-Cr-Al-Y alloy compositions were continued at 450°, 550°, 730°, 900°, and 1100°C. Most of the specimens are 0.76 mm thick with a surface area of 10 cm². All surfaces were cleaned by vapor blasting prior to testing. Weight change data for times up to 7000 hours at 900°C and 1100°C are shown in Figure 2.6. All the alloys which contain a nominal 1 percent yttrium exhibit comparable weight gains except the 1041 alloy which exhibits a high weight gain after 4000 hours at 1100°C. The alloys which contain low yttrium exhibit lower weight gains. This is attributed to the larger grain size of the low yttrium alloys which reduces the initial amount of internal grain boundary oxidation of yttrium.

Steam-Corrosion Studies

Steam corrosion tests of Fe-Cr-Al-Y alloys are being conducted at 550°, 730°, and 1100°C in low-pressure steam generated from deionized water. Sheet specimens having various surface pre-treatments are being tested.

Weight change data for several alloys tested for 4000 hours in 550°C and 730°C steam are presented in Table 2.4. As previously reported,⁹ the steam corrosion resistance of the alloys is improved by pre-oxidation in air at higher temperatures. In the non-pre-oxidized condition, the 1041 alloy exhibited the poorest corrosion resistance as indicated by the weight change data. The microstructure of the 1041 alloy after 1800 hours at 550°C is shown in Figure 2.7. Apparently the aluminum is oxidized internally and the chromium content is too low to form a protective surface oxide. The outer oxide, which cracks and spalls, is probably iron-rich. In the pre-oxidized condition, the corrosion resistance of the alloy is comparable to the 1541 and 2541 alloys.

⁹Ibid., pp. 21-23.

Fig. 2.6 - Weight gain as a function of test time at 900°C and 1100°C in static air for Fe-Cr-Al-Y alloys for times up to 7000 hours

Bright field illumination (Neg. 5315)

Polarized light (Neg. 5317)

Fig. 2.7 – Microstructure of surface oxides formed on 1041 alloy after 1800 hours at 550°C in steam (250X)

TABLE 2.4
WEIGHT GAIN DATA FOR PRE-OXIDIZED Fe-Cr-Al-Y ALLOYS
TESTED IN STEAM AT 550°C AND 730°C FOR 4000 HOURS

Alloy	Pre-Oxidation Treatment In Air			Steam Corrosion Testing (4000 hours)	
	Temperature, °C	Time, hr	Weight Gain, mg/cm ²	Temperature, °C	Weight Gain, mg/cm ²
2541	None			730	0.11
	980	125	0.18	730	0.00
	1100	125	0.54	730	-0.11
	1260	67	1.38	730	0.08
1541	None			730	0.52
	980	125	0.38	730	0.02
	1100	125	0.53	730	0.03
	1260	67	1.46	730	0.03
0561	None			550	0.79
	980	125	0.27	550	0.08
	1100	125	0.62	550	0.05
	1260	67	1.65	550	0.02
	None			730	0.25
	980	125	0.29	730	0.05
	1100	125	0.59	730	0.08
	1260	67	1.67	730	0.00
1041	None			550	5.90
	980	125	0.13	550	0.04
	1100	125	0.44	550	0.00
	1260	67	1.54	550	0.15
	None			730	4.48
	980	125	0.18	730	0.09
	1100	125	0.34	730	0.14
	1260	67	1.44	730	0.16

To evaluate the mechanical stability of the oxide formed at 980°C in air, sheet tensile specimens of the 1041 alloy were oxidized at this temperature, then plastically deformed prior to steam corrosion testing. One specimen was strained 1 percent at room temperature and another was strained 1 percent at 730°C. The specimens, together with a control specimen, were then exposed to 730°C steam for 1000 hours. Weight changes, about 0.3 mg/cm², and surface appearance were the same for all three specimens. An additional 1 percent strain was applied to the specimen previously strained 1 percent at room temperature, and all three specimens are on test for an additional 1000-hour corrosion cycle. These preliminary results indicate that small strains can be accommodated by the pre-oxidized surfaces.

Testing in the large steam rig at 730°C was continued on several alloys, some of which have accumulated over 4000 hours of test time. The current weight gain data for the alloys are presented in Table 2.5. The Fe-Cr-Al-Y alloys continue to exhibit lower weight gains than the nickel-base alloys and Type 446 stainless steel. Inconel 625, a potential superheat cladding alloy, was added to the testing program.

WORK PLANNED FOR NEXT PERIOD

Laboratory testing of Fe-Cr-Al-Y-clad fueled specimens for times up to 10,000 hours at 950°C and 1100°C in air will be continued. Specimens containing enriched UO₂ will be introduced into the test program as a more sensitive means of detecting uranium diffusion, using alpha count analyses. Additional tests will be conducted at 750°C to obtain compatibility data applicable to superheat reactors.

TABLE 2.5
WEIGHT GAIN DATA FOR ALLOYS TESTED AT 730°C IN STEAM

Alloy	Heat No.	No. Of Specimens	Surface Preparation	Test Time, hr	Weight Gain, mg/cm ²	
					Average	Spread
2541 + 1Nb	M-233	6	Vapor-blasted	2500	0.52	0.35 - 0.79
1541	M-231	4	Vapor-blasted	2900	0.51	0.34 - 0.85
1541	M-231	2	Vapor-blasted	4160	0.74	0.55 - 0.93
1541	MS-38	4	Vapor-blasted	2900	0.62	0.52 - 0.76
2541	MS-36	4	Vapor-blasted	2900	0.43	0.31 - 0.54
1041	M-239	3	Pre-oxidized at 980°C	1000	0.29	0.27 - 0.31
Inconel 600	-	1	Vapor-blasted	4160	0.97	-
Inconel 600	-	2	Pickled	4160	-	0.45 - 5.64
Incoloy 800	-	1	Vapor-blasted	4160	1.06	-
Incoloy 800	-	1	Pickled	4160	1.80	-
446 SS	-	6	Vapor-blasted	3400	0.83	0.56 - 1.25

The first in-pile test, LTFC-1, containing a 2541-clad Fe-UO₂ specimen, will be completed in the LITR after 1000 hours at 1100°C in flowing air. A second test cartridge will be prepared containing a 1541-clad Fe-UO₂ specimen.

The long-time corrosion testing of Fe-Cr-Al-Y alloys and selected commercial alloys will continue in both air and superheated steam. Metallographic examination and post-test ductility evaluations will be emphasized.

The determination of mechanical properties of the 1541 alloy and other experimental compositions will be continued with emphasis on correlations between chemical composition, structure, and ductility evaluations.

The study of irradiation effects on the properties, primarily ductility, will be continued. The ductile-to-brittle transition temperatures of the 1541 alloy after various treatments will be determined.

Studies on the mechanical stability of oxides formed during air-oxidation and subsequent behavior in steam will be continued.

3. HIGH-TEMPERATURE REACTOR MATERIALS RESEARCH

(57003)

The purpose of this program is to develop and evaluate methods of preparing and joining refractory metals and alloys and other high-temperature materials for use in fueled and non-fueled high-temperature, (1000° to 3000°C) reactor structural applications.

MECHANICAL PROPERTY EVALUATIONS

Arc-Cast Tungsten

Creep-rupture testing of arc-cast tungsten sheet specimens (0.15 cm thick, 0.6 cm wide, with a 2.54 cm gage length) in hydrogen was continued. The data accumulated to date from tests at 2200°, 2400°, 2600°, 2800°, and 3000°C are presented in Table 3.1.

All strain measurements for arc-cast tungsten were made with an optical extensometer¹ sighting on fiducial marks in the form of two 0.013-cm-diameter holes drilled completely through the gage section of the specimen with a spacing of 2.54 cm. Such fiducial marks were found to be quite satisfactory.²

Creep-Rupture - The stress-rupture data, presented in Figure 3.1, yield a straight line at constant temperature from 2000° to 2800°C when using logarithmic coordinates; the data also yield essentially parallel lines. Figure 3.2 presents the secondary (linear) creep rate versus stress plot which also yields straight lines at constant temperature when logarithmic coordinates are employed. These data, however, do not give parallel lines over the temperature range of 2000° to 2800°C, suggesting a possible change in the secondary creep mechanism.

Creep curves for the various temperatures and stresses are presented in Figure 3.3; in most cases these curves exhibit the conventional first, second, and third stages of creep. Deviations from the conventional creep curve occurred at 2000°C and stresses of 1.41 and 1.05 kg/mm² following annealing at 2000°C for 2 hours (see Figure 3.4); a slope change was observed in the region of 2 percent strain similar to that which normally occurs at the initiation of third-stage creep. At approximately 5 percent strain for the 1.05 kg/mm² test and at 10 percent for the 1.41 kg/mm² test, the creep rate decreased and again was linear followed by a third stage of creep and rupture. Such behavior suggested a structural change which was dependent on time at temperature as well as on stress. In an attempt to evaluate this behavior, a test was performed at 2000°C and 1.41 kg/mm² with prior annealing at 2400°C for 1 hour. This test (Figure 3.4) exhibited the conventional creep curve, although the linear creep rate was lower, and the time-to-rupture greater, than for the test at the same conditions with prior annealing at 2000°C for 2 hours. The fact that the specimen annealed at 2400°C showed a greater strain in

¹"High-Temperature Materials Program Progress Report No. 35, Part A," GE-NMPO, GEMP-35A, May 28, 1964, p. 3.

²"Fourth Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume 1 - Materials," GE-NMPO, GEMP-334A, February 26, 1965, pp. 21-23.

TABLE 3.1
CREEP-RUPTURE RESULTS FOR ARC-CAST TUNGSTEN FROM 1600° TO 3000°C IN HYDROGEN^a

Specimen No. For W(3) Material ^b	Test Conditions			Time To Indicated Elongation, hr								Rupture Elongation, %	Linear Creep Rate, min ⁻¹
	Temperature, °C	Stress, kg/mm ²	Atmosphere	0.2%	0.5%	1%	2%	3%	5%	10%	Rupture		
47	1600	3.37	Hydrogen	0.08	0.80	2.90	11.6	21.9	45.5	76.8	137 ^c	-	1.4×10^{-5}
48	1600	4.22	Hydrogen	-	-	0.15	1.40	3.35	9.70	16.0	30.9	76	5.1×10^{-5}
45	2000	1.05	Hydrogen	0.12	1.70	6.30	16.5	25.2	45.3	101	256	56	1.5×10^{-5}
39	2000	1.41	Hydrogen	-	0.80	2.50	6.10	8.25	11.0	16.2	63.1	94	9.2×10^{-5}
46	2000 ^d	1.41	Hydrogen	-	0.17	0.65	2.80	6.10	14.4	35.1	100	92	3.9×10^{-5}
16	2200	0.70	Hydrogen	0.12	1.33	5.00	14.5	25.0	46.5	95.0	237	125	1.5×10^{-5}
15	2200	0.84	Hydrogen	0.01	0.41	1.90	6.45	11.8	22.3	48.0	119	86	3.1×10^{-5}
14	2200	1.05	Hydrogen	-	0.05	0.35	1.58	3.30	6.60	14.8	40.7	106	9.6×10^{-5}
40	2200	1.26	Hydrogen	-	-	0.10	0.52	1.18	2.60	-	3.35 ^c	-	2.3×10^{-4}
13	2200	1.41	Hydrogen	-	-	0.02	0.20	0.51	1.30	3.30	7.72	74	4.0×10^{-4}
22	2400	0.46	Hydrogen	0.05	0.50	2.12	6.00	9.80	18.5	40.0	146	102	3.9×10^{-5}
24	2400	0.56	Hydrogen	-	0.17	0.80	2.70	5.00	9.75	21.3	61.4	120	7.0×10^{-5}
21	2400	0.70	Hydrogen	-	0.02	0.18	0.78	1.52	3.18	7.40	17.5	83	2.0×10^{-4}
17	2400	0.84	Hydrogen	-	0.004	0.05	0.28	0.60	1.40	3.42	9.25	73	4.0×10^{-4}
38	2400	1.05	Hydrogen	-	-	0.01	0.08	0.20	0.50	1.30	3.09	86	1.0×10^{-3}
27	2600	0.28	Hydrogen	0.12	0.71	2.30	6.30	10.5	19.2	41.0	123	84	3.8×10^{-5}
26	2600	0.35	Hydrogen	0.03	0.17	0.64	1.97	3.45	6.60	14.0	43.4	87	1.1×10^{-4}
33	2600	0.46	Hydrogen	-	0.04	0.20	0.71	1.32	2.62	5.60	15.0	104	2.6×10^{-4}
25	2600 ^f	0.56	Argon	-	-	0.02	0.12	0.28	0.67	1.62	4.77 ^e	64	8.5×10^{-4}
19	2600	0.84	Hydrogen	-	-	-	0.004	0.02	0.08	0.25	0.78	78	5.0×10^{-3}
34	2800	0.18	Hydrogen	0.33	1.48	4.00	12.0	22.0	45.0	79.0	144	40	1.5×10^{-5}
36	2800	0.21	Hydrogen	0.06	0.33	1.18	3.40	6.30	13.4	28.8	51.9	46	4.9×10^{-5}
29	2800	0.28	Hydrogen	-	0.03	0.12	0.55	1.14	2.50	5.60	14.0	74	2.4×10^{-4}
28	2800	0.35	Hydrogen	-	-	0.01	0.10	0.28	0.58	1.61	4.30	64	8.3×10^{-4}
49	3000 ^f	0.21	Argon	-	0.01	0.03	0.11	0.22	0.51	1.82	2.80	22	6.7×10^{-4}

^aAll specimens were annealed for 2 hours at test temperature in hydrogen prior to test.

^bAll W(3) specimens are 0.15 cm thick, 0.6 cm wide, and 2.54 cm in gage length.

^cTest terminated, no rupture.

^dAnnealed for 1 hour at 2400°C in hydrogen prior to test.

^eSpecimen rotated at 4.1 hours, affecting rupture time.

^fTested in argon.

Fig. 3.1 – Stress-rupture data for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen

Fig. 3.2 – Linear creep rate data for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen

Fig. 3.3—Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen

Fig. 3.3 (Cont.) – Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen

Fig. 3.4—Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested at 2000°C in hydrogen.

the first stage of creep suggests that the structure was less creep-resistant until strain-hardening became predominant. Creep data for tests from 2200°C to 3000°C showed the conventional creep curve, indicating that annealing for 2 hours at test temperature was sufficient to stabilize the structure.

Figure 3.5 presents the results of elongation-at-rupture versus temperature for various stresses and thereby gives an indication of the ductility at temperature for arc-cast tungsten. Maximum elongation at rupture occurs at 2200°C and 2400°C with a decrease above and below these temperatures.

Previously reported stress-rupture and creep data³ for both tungsten and molybdenum showed that wrought-powder metallurgy materials purchased from different vendors give varying results. Arc-cast molybdenum purchased from four vendor sources gave essentially identical results for rupture times from 0.1 to 1000 hours when creep-rupture tested at 2200°C. The reason for the difference in stress-rupture and creep results from different sources for powder metallurgy molybdenum has not yet been determined. Results from arc-cast materials are more representative of the basic properties of the material. A further confirmation of this is shown in Figure 3.6 where an isochronal stress-rupture plot of stress versus temperature for both arc-cast molybdenum and arc-cast tungsten is presented. On the basis of homologous temperature, both tungsten and molybdenum give essentially identical rupture curves from 50 to 85 percent of the absolute melting temperature and rupture times from 0.1 to 100 hours.

³Ibid., Table 1.2, p. 33.

Fig. 3.5 - Elongation at rupture versus temperature for 0.15-cm-thick arc-cast tungsten sheet tested in hydrogen

Fig. 3.6 - Isochronal plot of stress-rupture data for arc-cast tungsten and molybdenum

In view of the reproducibility of arc-cast material, Larson-Miller curves are presented in Figure 3.7 for 1, 3, 5, and 10 percent strain and rupture for arc-cast tungsten. The data taken from Table 3.1 which cover the results of tests from 1600° to 3000°C and rupture times from 0.8 to 144 hours.

Fig. 3.7 – Larson-Miller parameter for arc-cast tungsten tested from 1600° to 3000°C

Photographs of typical specimens tested at 2200°, 2400°, 2600°, and 2800°C are given in Figures 3.8 and 3.9. Fracture at the holes occurred after test on removal of specimens from the tungsten pins. The figures show the general "orange peel" appearance due to strain. The straining in the gage section (0.15 by 0.63 by 2.54 cm) was quite uniform at 2200°C and 2400°C but some reduction in area was observed in the region of the fracture at 2600°C and 2800°C. This reduction appears to be related to the elongation-at-rupture-versus-temperature curve shown in Figure 3.8. The fracture at rupture appeared to be transgranular.

Figures 3.10 through 3.13 are photomicrographs of typical specimens after test. The material is single-phase, exhibiting large grains. These specimens also contained numerous substructure grains with wide variation in size. Some appear equiaxed and are located within the larger grains. Others appear to exist within larger fibrous-type grains oriented at an angle to the surface of the specimens. Inter- and intragranular pores were noted randomly throughout the specimens with the greater quantity occurring at the higher temperatures and longer times.

First-Stage Creep - Creep curves for the arc-cast tungsten material tested at 2400°C under five different stresses are shown in Figure 3.14, where a small arrow indicates the approximate beginning of the second stage of creep. These same creep data are shown in Figure 3.15 on a log-log plot. This type of presentation reveals the striking similarity

Temperature, °C			
2200	2200	2400	2400
Stress, kg/mm ²			
1.41	0.70	1.05	0.46
Time, hr			
7.7	237	3.1	146
Elongation, %			
75	125	86	102

Fig. 3.8 – Arc-cast tungsten specimens after creep-rupture testing at 2200°C and 2400°C, shown approximately half-size (Neg. P65-2-17A)

Temperature, °C			
2600	2600	2800	2800
Stress, kg/mm ²			
0.84	0.28	0.35	0.18
Time, hr			
0.8	123	4.3	144
Elongation, %			
78	84	64	40

Fig. 3.9 – Arc-cast tungsten specimens after creep-rupture testing at 2600°C and 2800°C, shown approximately half-size (Neg. P65-2-17B)

Fig. 3.10 – Section of arc-cast tungsten after 237 hours at 2200°C and 0.70 kg/mm² stress (Neg. 5657, 50X, etched)

Fig. 3.11 – Section of arc-cast tungsten after 146 hours at 2400°C and 0.46 kg/mm² stress (Neg. 5659, 50X, etched)

Fig. 3.12 – Section of arc-cast tungsten after 0.78 hours at 2600°C and 0.84 kg/mm² stress (Neg. 5660, 50X, etched)

Fig. 3.13 – Section of arc-cast tungsten after 144 hours at 2800°C and 0.17 kg/mm² stress (Neg. 5665, 50X, etched)

Fig. 3.14 – Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested at 2400°C in hydrogen

Fig. 3.15 – Creep curves for 0.15-cm-thick arc-cast tungsten sheet tested at 2400°C

of the creep curves at various stresses, an observation not possible when only the type of plot shown in Figure 3.14 is studied. Figures 3.16 and 3.17 present additional logarithmic plots for tests at 2600°C and 2800°C. The type of plot used in Figure 3.15 is not completely satisfactory since it does not present identification of the beginning of second-stage creep; i. e., the linear portions of the creep curves in Figure 3.14 are not linear when logarithmic coordinates are employed. For this reason, the arrows from Figure 3.14 were employed to indicate the initiation of the second stage of creep.

A desirable feature of the type of plot shown in Figure 3.15, aside from comparison of creep curves at various stresses for a given temperature, relates to first-stage creep analysis. Ordinarily, a parabolic creep law of the form:

$$\epsilon = bt^m + \epsilon_0 \quad (1)$$

applies to first-stage creep behavior where ϵ is the instantaneous strain, ϵ_0 is the strain immediately following load application, t is the time, and b and m are constants. Obviously, when ϵ_0 is negligible (it can never be zero) the parabolic law describes a linear relationship for first-stage creep behavior when strain and time are both plotted on logarithmic scales. Nonlinearity on such a plot in the first stage of creep results when ϵ_0 assumes values which are no longer negligible. In these cases, a replotting of the data in terms of $\epsilon - \epsilon_0$ versus time on logarithmic coordinates is dictated to obtain linearity. Then the slope of this line yields the exponent of time in the parabolic creep law. Such an analysis, described by Hazlett and Parker,⁴ has been applied to various materials. Identification of the value of ϵ_0 is said to result from strain measurements in the early moments following load application which permits an extrapolation to zero time to obtain ϵ_0 . Since such data are not always obtainable, a trial and error approach was proposed by the authors in which values of ϵ_0 were assumed until the logarithmic plot of $\epsilon - \epsilon_0$ versus time was linear.

A recently proposed analytical procedure⁵ for the calculation of ϵ_0 eliminates the need for the previously mentioned trial and error approach. Two values of time are selected and the corresponding strain values read from the creep curve. Then a third value of time, equal to the geometric mean of the t_1 and t_2 values, is selected thus:

$$t_3 = \sqrt{t_1 t_2} \quad (2)$$

Substitution in:

$$\epsilon_0 = \frac{\epsilon_3^2 - \epsilon_1 \epsilon_2}{2\epsilon_3 - \epsilon_1 - \epsilon_2} \quad (3)$$

allows a direct calculation of the ϵ_0 values for cases where the parabolic creep law applies. Application of this procedure to the 2400°C data of Figure 3.15 yields the results shown in Figure 3.18. As noted, excellent linearity is obtained and the slopes are all essentially constant at about 0.6. Values for ϵ_0 are listed along with each test condition.

It is evident in Figure 3.18 that deviations from linearity occur with the initiation of second-stage creep. This behavior is observed in every case and always results in a curve which is concave upward in this region. Such behavior is in accord with the recognized differences between the first- and second-stage creep.

Plots of strain versus t^m on rectangular coordinates are also linear for certain materials under certain conditions, and may be extrapolated to zero time to obtain the value

⁴T. H. Hazlett and E. R. Parker, "Nature of the Creep Curve," *Journal of Metals*, Vol. 5, 1953, p. 318.

⁵J. B. Conway, "Calculation of ϵ_0 From First Stage Creep Data," submitted to Transactions AIME as Letter to the Editor. (GE-NMPO, February 1965.)

Fig. 3.16 – Creep curves for 0.15-cm-thick arc-cast tungsten at 2600°C

Fig. 3.17 – Creep curves for 0.15-cm-thick arc-cast tungsten at 2800°C

Fig. 3.18 – Creep curve ($\epsilon - \epsilon_0$) for 0.15-cm-thick arc-cast tungsten sheet tested at 2400°C, showing linearity during first stage of creep

for ϵ_0 . Such plots for the 2400°C data of Figure 3.15 are shown in Figure 3.19 for a value of $m = 0.6$. This value of m was obtained from the plot shown in Figure 3.18 and the strain values for the first stage of creep are seen to be described quite adequately in this fashion. At 2400°C, and for the stresses involved, the exponent of 0.6 was found to apply to these tungsten data quite satisfactorily since linearity is observed up until the beginning of second-stage creep. Deviations from linearity, however, are noted at low strain values when the exponent of 0.6 is employed, suggesting that a single value of the exponent cannot accurately describe the strain - time relations over the entire first stage of creep. Such deviations also preclude the attachment of any significant meaning to the ϵ_0 value obtained by extrapolating this plot to zero time. It is interesting that when $m = 0.5$, a plot similar to Figure 3.19 is obtained which is also linear and gives a better representation of the data in the early portion of the first stage of creep. However, in this case, the linearity does not persist throughout the entire first stage, confirming the statement made above that a parabolic creep law with a single value for the exponent is not completely adequate in describing these data.

Plots similar to Figure 3.18 need not be prepared to evaluate m for use in the rectangular plot of Figure 3.19 since special analytical procedures are available for this purpose. For example, de Lacombe⁶ has described a finite difference approach which leads to a direct calculation of the exponent of time in the first-stage creep equation. In this procedure, time values are selected in geometric progression and tabulated along with the corresponding values of strain obtained from the creep curve. Then a plot is made of the difference ($\epsilon_{i+1} - \epsilon_i$) versus t_i on logarithmic coordinates. Basic finite difference relationships indicate this to be linear with a slope equal to the value of m . It can also be shown that the m value can be obtained without resorting to the logarithmic plot of ($\epsilon_{i+1} - \epsilon_i$) versus time. Actually, for an equation of the type applicable to first-stage

⁶J. de Lacombe, "A Method of Representing Creep Curves," *Rev. Metal.*, Vol. 36, 1939, p. 178.

Fig. 3.19 – Strain versus $t^{0.6}$ for 0.15-cm-thick arc-cast tungsten sheet at 2400°C; showing linearity during first stage of creep

creep, and when the time values are arranged in geometric progression, it can be shown that the values for the ratio of successive strain differences, expressed by:

$$\frac{\epsilon_{i+2} - \epsilon_{i+1}}{\epsilon_{i+1} - \epsilon_i}$$

will also be in geometric progression. In other words, this ratio will be constant throughout the first-stage creep range and will be equal to r^m where r is the constant value in the geometric progression $t_i = r^i t_0$. This approach is demonstrated in Table 3.2. For the data at 0.70 kg/mm² (from Figure 3.15), the ratio of successive differences is reasonably constant and, since the times have been arranged in a geometric progression with a value of $r = 1.3$, the value of m obtained from Table 3.2 averages close to 0.6, indicating excellent agreement with the slope obtained in Figure 3.18. However, it should be noted that, consistent with the above remarks, the value of m obtained at the lower time values deviates from 0.6.

First-stage creep analyses similar to those illustrated in Figure 3.19 were also completed for the data obtained at other stresses and temperatures. A correlation of the ϵ_0 and b values with stress and temperature was partially completed with fairly satisfactory results. For example, as shown in Figure 3.20, a plot of b versus stress is linear on logarithmic coordinates to yield a relation of the type:

$$b = \bar{a} \sigma^{\bar{c}} \quad (4)$$

A point of interest is that such plots for the four temperatures studied are parallel, indicating a $\bar{c}$ value independent of temperature. A plot of $\bar{a}$ versus temperature, shown in Figure 3.21, was found to be linear on semi-logarithmic coordinates to yield a relationship of the form:

$$\bar{a} = \bar{d} e^{\bar{g} T} \quad (5)$$

TABLE 3.2
ILLUSTRATION OF de Lacombe
CALCULATION PROCEDURE BASED ON
FINITE DIFFERENCES^a

t_i , min.	ϵ_i , cm/cm	$\frac{\epsilon_{i+2} - \epsilon_{i+1}}{\epsilon_{i+1} - \epsilon_i}$	
		$\epsilon_{i+1} - \epsilon_i$	$\epsilon_{i+2} - \epsilon_{i+1}$
1.00	0.0050	0.0002	
1.30	0.0052	0.0003	1.50
1.69	0.0055	0.0004	1.33
2.20	0.0059	0.0004	1.00
2.86	0.0063	0.0005	1.25
3.72	0.0068	0.0006	1.20
4.84	0.0074	0.0008	1.33
6.29	0.0082	0.0008	1.00
8.18	0.0090	0.0010	1.25
10.63	0.0100	0.0012	1.20
13.82	0.0112	0.0015	1.25
17.97	0.0127	0.0017	1.13
23.36	0.0144	0.0020	1.18
30.37	0.0164	0.0022	1.10
39.48	0.0186	0.0028	1.27
51.32	0.0214	0.0034	1.21
66.72	0.0248	0.0043	1.26
86.74	0.0291		

^aData for arc-cast tungsten at 2400°C and a stress of 0.7 kg/mm². Time in geometric progression.

Such correlations lead to the following equation for calculating the first-stage strain at various times for arc-cast tungsten tested at temperatures from 2200° to 2800°C:

$$\epsilon = \bar{de}^{\bar{g}T} \bar{\sigma}^{\bar{c}} t^m + \epsilon_0 \quad (6)$$

$$\epsilon = 1.77 \times 10^{-12} e^{8.24 \times 10^{-3} T} \sigma^{3.34} t^{0.6} + \epsilon_0 \quad (7)$$

where:

ϵ = strain

T = °K

σ = kg/mm²

t = minutes

Presently, specific values of ϵ_0 , corresponding to a given temperature and stress, must be employed with this equation. A correlation of ϵ_0 similar to that employed for b is now in progress in an attempt to develop a fairly general equation for this material to express first-stage creep behavior.

During the course of the above first-stage creep analyses, special consideration was given to the Andrade⁷ one-third law to determine the extent of its applicability to the arc-cast tungsten data. The Andrade creep equation,

$$l = l_0 (1 + \beta t^{1/3}) e^{kt} \quad (8)$$

written in terms of strain:

$$1 + \epsilon = \frac{l_0 (1 + \beta t^{1/3}) e^{kt}}{l'} \quad (9)$$

⁷E. N. daC. Andrade, "On the Viscous Flow in Metals and Allied Phenomena," *Proceedings of the Royal Society*, Vol. 84, 1910, p. 1.

Fig. 3.20 – Plot of “b” versus stress showing constant slope “c” for arc-cast tungsten from 2200° to 2800°C

where ℓ is the instantaneous length, ϵ the instantaneous strain, t the time, ℓ' the specimen length before load application, ℓ_0 the specimen length immediately after load application, and β and k are constants, yielded excellent results. Initially, an analytical approach based on a quadratic solution was employed to calculate the Andrade creep equation constants. Three equally spaced values of time were selected and the corresponding values of strain were read from the creep curve. Substitution in the Andrade-type equation and re-arranging gave the quadratic expression:

$$e^{2ka} \left[L_{12} L_{23} (t_2)^{1/3} - L_{12} L_{23} (t_3)^{1/3} \right] + e^{ka} \left[L_{23} (t_3)^{1/3} - L_{23} (t_1)^{1/3} \right] + \left[(t_1)^{1/3} - (t_2)^{1/3} \right] = 0 \quad (10)$$

where a is the interval between selected time values, L_{12} is the ratio of $(1 + \epsilon)$ values at t_1 and t_2 , and L_{23} is a similar ratio for t_2 and t_3 . Direct solution yields the value for k and then β and ℓ_0 values.

Another calculation procedure for obtaining Andrade-type creep equation constants has been proposed⁸ based on a special least-squares procedure. This technique has the advantage that it treats all the experimental points simultaneously and hence avoids the possible

⁸J. B. Conway, “A Least Squares Technique for Calculating Andrade Creep Equation Constants,” submitted for presentation at AIME Fourth Symposium on Refractory Metals, French Link, Indiana.

Fig. 3.21 – Plot of “ $\dot{\epsilon}$ ” versus temperature showing linearity for arc-cast tungsten from 2200° to 2800°C

bias which might arise in the quadratic approach by having the constants depend on only three of the experimental points. The results obtained at 2400°C by employing this least-squares procedure and the creep curves calculated using these constant values are presented later in this discussion.

Another creep analysis technique which is fairly satisfactory involves development of an equation relating strain and time which will apply accurately throughout both the first and second stages of creep. In this approach an equation of the form:

$$\epsilon = f + gt - he^{-pt} \quad (11)$$

is used where f , g , h , and p are all positive constants. Obviously, the first two terms describe the linear (secondary) creep rate with the value of f being obtained by extrapolating the linear portion of the creep curve to a time equal to zero. The last term is then a correction term for the first stage of creep and the constants are so adjusted to render this term

completely negligible for time values exceeding those corresponding to the initiation of second-stage creep. Constants for this third term are evaluated by obtaining the vertical differences between an experimental strain value in first-stage creep and the line obtained by extrapolating the linear portion of the creep curve back to zero time. When these differences are plotted versus time on semi-logarithmic coordinates, a straight line should result from which the constants h and p can be evaluated. Such a plot for arc-cast tungsten at 2400°C and 0.84 kg/mm^2 is shown in Figure 3.22. Excellent linearity is seen to exist and yields the following equation (t in minutes):

$$\epsilon = 0.0155 + 4.08 \times 10^{-4} t - 0.0082 e^{-0.072t} \quad (12)$$

For these particular conditions, this equation allows the strain to be calculated for any time value within the first and second stages of creep. Similar relations have been obtained for the other test conditions. In each case a definite deviation from linearity was noted involving the first few minutes of the creep test. Apparently a different creep mechanism is operating in these few moments following load application. Additional studies in this area are being considered.

Fig. 3.22 – Analysis of the equation, $\epsilon = f + gt - he^{-pt}$, for arc-cast tungsten data at 2400°C and 0.84 kg/mm^2

In summary, the creep data obtained to date for arc-cast tungsten at various stresses at temperatures of 2200°, 2400°, 2600°, 2800° and 3000°C were analyzed to develop strain - time equations of the following forms:

$$\epsilon = a + bt^{0.6} \text{ (first stage only)} \quad (13)$$

$$\epsilon = c + dt^{0.5} \text{ (portion of first stage only)} \quad (14)$$

$$\epsilon = \frac{\ell_0 (1 + \beta t^{1/3}) e^{kt}}{\ell'} - 1 \text{ (first stage only)} \quad (15)$$

$$\epsilon = f + gt - he^{-pt} \text{ (first and second stage)} \quad (16)$$

Values obtained for these constants in the analyses made to date are presented in Table 3.3. Also indicated in this summary table are:

ϵ_I - the value of strain at the end of stage 1

ϵ_{II} - the value of strain at the end of stage 2

t_I - the time corresponding to the end of stage 1

t_{II} - the time corresponding to the end of stage 2

and ϵ'_I - the strain in stage 1 to which the $t^{0.5}$ expression applies

A few examples of the excellent degree to which the constants in Table 3.3 actually describe the experimental data are presented in Figure 3.23. In essentially all cases the agreement is within a few percent and well within experimental scatter.

X-ray Diffraction and Electron Microscopy Studies of Arc-Cast Molybdenum

Creep-rupture tests of arc-cast molybdenum rods at 2200°C were previously reported and compared to the results obtained from arc-cast molybdenum sheet.⁹ The creep-rupture properties were identical, indicating no surface-to-volume ratio effect with surface-to-volume ratios from 25 to 190. Typical rod specimens, after test, were then made the subject of a substructure study by X-ray diffraction and optical microscopy. Figure 3.24 shows three of the rod specimens (0.4 cm in diameter) tested in hydrogen at 2200°C and stresses of 0.32, 0.20, and 0.14 kg/mm², with times-to-rupture of 2.66, 17.0, and 145.2 hours, respectively. Prior to testing, the specimens were annealed at 2200°C for 2 hours in hydrogen. Figures 3.24a and 3.24b illustrate the characteristic necking prior to rupture, while Figure 3.24c is a good example of deformation along preferred glide planes similar to that reported for other materials.

The tested specimens were sectioned transversely and longitudinally with respect to the direction of the applied stress as well as parallel to the apparent glide plane. The longitudinal section was ground down to the plane of the knife-edge of the fracture. As a reference, an additional rod specimen was annealed at 2200°C for 2 hours in hydrogen. Sections were also cut transversely and longitudinally with respect to the gage length for the reference specimen.

The pieces were then electro-polished and electro-etched in an electrolyte of 6 parts methanol to 1 part sulfuric acid. Representative areas from each section were photographed. The same area was examined by the X-ray diffraction back-reflection method.

The information gained from these pieces is mainly in the form of observations. As shown in Figure 3.25, the reference material exhibited large equiaxed grains containing numerous dislocation etch pits. Photomicrographs and back-reflection photographs of the same transverse sections of the tested specimens are shown in Figures 3.26, 3.27, and 3.28. The 0.32 kg/mm² sample was highly polygonized, containing small subgrains with

⁹"High-Temperature Materials Program Progress Report No. 43, Part A," GE-NMPO, GEMP-43A, January 29, 1965, p. 25.

TABLE 3.3
CONSTANTS FOR USE IN VARIOUS CREEP EQUATION FORMS FOR ARC-CAST TUNGSTEN

$$\epsilon = a + bt^{0.6}, \quad \epsilon = c + dt^{0.5}, \quad \epsilon = f + gt - he^{-pt}, \quad \text{and} \quad \epsilon = \ell'_0 (1 + \beta t^{1/3}) e^{kt} - 1^*$$

Specimen No. For W(3) Material	Temperature, °C	Stress, kg/mm ²	ϵ_I	ϵ_{II}	t_I	t_{II}	ϵ'_I	a	b	c	d	ℓ'_0	$\beta \times 10^3$	$k \times 10^5$	f	g	h	p
22	2400	0.46	0.012	0.089	180	2520	0.007	0.00125	0.000472	0.00085	0.000727	1.00062	1.05	3.251	0.0067	3.28×10^{-5}	0.0044	0.0134
24	2400	0.56	0.014	0.089	210	1140	0.008	0.0017	0.0008	0.0012	0.00122	1.00076	1.66	6.74	0.0089	7.02×10^{-5}	0.0060	0.0238
21	2400	0.70	0.023	0.086	60	375	0.015	0.0031	0.00169	0.0021	0.00248	1.00173	2.975	16.16	0.0118	1.99×10^{-4}	0.0063	0.0421
17	2400	0.84	0.040	0.101	60	216	0.022	0.0037	0.00303	0.0028	0.00417	1.00135	5.32	28.99	0.0155	4.08×10^{-4}	0.0080	0.072
38	2400	1.05	0.040	0.108	20	85	0.03	0.0068	0.00531	0.0045	0.00727	1.00189	9.46	54.91	0.019	1.04×10^{-3}	0.0085	0.153
34	2800	0.18	0.027	0.055	1140	3120	-	0.000	0.000374	-	-	-	-	-	-	-	-	-
36	2800	0.21	0.024	0.075	270	1320	-	0.0003	0.000791	-	-	-	-	-	-	-	-	-
29	2800	0.28	0.028	0.079	60	270	-	0.00258	0.00215	-	-	-	-	-	-	-	-	-
28	2800	0.35	0.025	0.084	12	81	-	0.0073	0.00428	-	-	-	-	-	-	-	-	-
27	2600	0.28	0.018	0.116	300	2880	-	0.0005	0.000498	-	-	-	-	-	-	-	-	-
26	2600	0.35	0.024	0.087	150	780	-	0.0003	0.00111	-	-	-	-	-	-	-	-	-
33	2600	0.46	0.025	0.056	60	180	-	0.0017	0.00177	-	-	-	-	-	-	-	-	-
25	2600	0.56	0.036	0.139	24	144	-	0.005	0.00459	-	-	-	-	-	-	-	-	-
19	2600	0.84	0.048	0.086	4.5	12	-	0.014	0.0129	-	-	-	-	-	-	-	-	-
15	2200	0.84	0.015	0.080	240	2280	-	0.00165	0.00049	-	-	-	-	-	-	-	-	-
14	2200	1.05	0.029	0.070	180	600	-	0.00285	0.00117	-	-	-	-	-	-	-	-	-
40	2200	1.27	0.025	0.140	48	114	-	0.0092	0.00198	-	-	-	-	-	-	-	-	-
45	2000	1.05	0.009	0.018	300	900	-	0.0011	0.000271	-	-	-	-	-	-	-	-	-
39	2000	1.41	0.008	0.020	90	360	-	0.0006	0.000445	-	-	-	-	-	-	-	-	-
46	2000	1.41	0.030	0.112	360	2400	-	0.0025	0.000802	-	-	-	-	-	-	-	-	-

*where:

$$\ell'_0 = \frac{\ell_0}{\ell'}$$

ϵ = strain

t = time, minutes

Fig. 3.23—Experimental first-stage creep data for 0.15-cm-thick arc-cast tungsten sheet at 2400°C shown in comparison to curves calculated using constants in Table 3.3 (experimental points given as circles)

(a) 0.32 kg/mm² stress, 2.66 hours to rupture (Neg. 5590)

(b) 0.20 kg/mm² stress, 17.0 hours to rupture (Neg. 5588)

(c) 0.14 kg/mm² stress, 145.2 hours to rupture (Neg. 5587)

Fig. 3.24 – Creep-rupture specimens of arc-cast molybdenum rods (0.4 cm in diameter) after testing at 2200°C in hydrogen (7X)

(a) Longitudinal section (Neg. 5683)

(b) Transverse section (Neg. 5681)

Fig. 3.25 – Arc-cast molybdenum rod after annealing at 2200°C for 2 hours in hydrogen (100X, etched)

(a) (Neg. 5554, 100X, etched)

(b) (Neg. M7571T)

Fig. 3.26 — Photomicrograph and Lave pattern for the same transverse section of an arc-cast molybdenum rod after 2.66 hours (rupture) at 2200°C and 0.32 kg/mm² stress

(a) (Neg. 5546, 100X, etched)

(b) (Neg. M7570T)

Fig. 3.27 – Photomicrograph and Lave pattern for the same transverse section of an arc-cast molybdenum rod after 17 hours (rupture) at 2200°C and 0.20 kg/mm² stress

(a) (Neg. 5539, 100X, etched)

(b) (Neg. M7569T)

Fig. 3.28 – Photomicrograph and Lave pattern for the same transverse section of an arc-cast molybdenum rod after 145.2 hours (rupture) at 2200°C and 0.14 kg/mm² stress

relatively large tilt-angle boundaries. As the time-to-rupture increased, polygonization decreased and the grain size increased. For the longest time, a single crystal had grown to span the entire cross section. The back-reflection photographs clearly reveal the differences in the subgrain structure of these specimens and the strong $[110]$ orientation.

In all of the longitudinal sections, the orientation was primarily $[001]$ with a strong $\langle 110 \rangle$ directionality along the axis of applied stress. The extreme polygonization and $[001]$ orientation of the 0.32 kg/mm^2 sample is demonstrated by the Laue pattern reproduced in Figure 3.29. The general appearance of a typical longitudinal section for the 0.20 kg/mm^2 specimen is shown in Figure 3.30. This shows that the longitudinal sections are consistent with the transverse sections in that the short-time test piece was extremely polygonized, but the degree of polygonization decreased as time-to-rupture increased.

Diagonal sections were cut along the apparent glide planes illustrated in Figure 3.24c. The 0.32 kg/mm^2 specimen was drastically polygonized as shown in Figure 3.31 and the orientation could not be determined from the back-reflection photograph. The other two specimens, showing much less polygonization, were found to exhibit a strong $[110]$ orientation.

The major points of interest derived from these results are:

1. The slip planes for molybdenum at 2200°C are $\{110\}$, as expected. It was not possible to determine the slip direction. Further work will be done to confirm that slip takes place in the expected $\langle 112 \rangle$ direction.

Fig. 3.29 – Laue pattern from longitudinal section of an arc-cast molybdenum rod after rupture at 2200°C and 0.32 kg/mm^2 stress (Neg. M7571L)

Fig. 3.30 – Longitudinal section of arc-cast molybdenum rod after rupture at 2200°C and 0.20 kg/mm² stress (Neg. 5548, 250X, etched)

Fig. 3.31 – Diagonal section of arc-cast molybdenum rod after rupture at 2200°C and 0.32 kg/mm² stress (Neg. 5558, 50X, etched)

2. The high-stress, short-time-to-rupture samples were very highly polygonized with dislocation etch pits outlining the subgrain boundaries. At the intermediate stress level, polygonization decreased and the number of random individual dislocations increased. At the lowest stress and longest time, the dislocations were still random but much fewer in number. These changes are illustrated in Figure 3.32 for diagonal sections cut along slip planes.

Creep Measurements with an Electro-Optical Extensometer

The present technique employed at GE-NMPO in measuring the creep characteristics of refractory metals at high temperatures (1600° to 2800°C) consists of manually reading and recording strain with a twin optical extensometer. While excellent primary and secondary stage creep results can be obtained by using the twin optical extensometer, precise primary-stage strain or tensile strain cannot be observed and recorded accurately for high rates of strain. Concurrent with the regular creep-rupture program, an evaluation was completed on an electro-optical extensometer (Optron) for use in making strain measurements. The Optron can continuously measure and record strain rates up to 5000 cm/cm-sec, with a resolution of 10^{-4} cm, and an accuracy within 2 percent. It, therefore, may be used for strain measurements in tensile, compression, and creep tests at high temperatures, providing satisfactory fiducial marks are used.

The Optron is an electro-optical instrument which follows the motion of a fiducial mark optically. For creep measurements, two instruments (trackers) are used and the electrical outputs are summed to produce an indicated strain between the two finite marks. A schematic of an individual tracker is shown in Figure 3.33. The target image is projected on the image dissector tube by the lens system. The light (photon) image striking the cesium coated dissector tube produces electrons which are focused on an aperture in front of the multiplier stage. When the system is balanced to a reference voltage and is mechanically at zero with respect to the target, there is no output to the deflection yoke. As the target moves, the optical image is displaced. In order to maintain a reference voltage in the amplifier, the electron image is displaced back to its original position by applying a voltage to the deflection yoke. The target motion is therefore proportional to the deflection yoke voltage. When two trackers are used, the deflection voltage output of each is summed electrically producing a voltage proportional to the displacement between the two targets. Figure 3.34 shows the Optron and associated equipment.

Since the trackers detect a sharp demarkation between light and dark, any projections on the test sample which give a suitable contrast can be used as targets. At temperatures below 600°C, two painted black bands suffice as targets. Any projections on the test sample when viewed through the furnace appear bright at high temperatures and contrast is obtained by viewing past the sample through the furnace heating element and radiation shields onto the cold furnace wall. For the measurement of creep in sheet samples, several target designs (projections) were evaluated, but 0.05-cm-diameter by 0.32-cm-long tungsten wires, electron-beam-welded perpendicular to the surface of the sample, produced the most satisfactory results (Figure 3.35). When viewed through the furnace, these pins appear as two bright horizontal lines on a black background.

In addition to the numerous bench tests and calibrations, 14 creep tests of arc-cast molybdenum at 1800°C and 2200°C were performed using the Optron for the measurement of strain. Table 3.4 lists the test conditions and results obtained. The first few specimens were tested to rupture to determine if the targets and/or the welding had any adverse effects on the sample. For these tests, fracture occurred at or near the center of the samples. The secondary (linear) creep rates, stress-rupture life, and percent elongations at rupture were within the normal scatter of similar tests performed without the targets used for the Optron, when tested at the same conditions. The remaining tests were run long enough to

(a) 0.32 kg/mm² stress, 2.66 hours to rupture (Neg. 5560)

(b) 0.20 kg/mm² stress, 17.0 hours to rupture (Neg. 5552)

(c) 0.14 kg/mm² stress, 145.2 hours to rupture (Neg. 5544)

Fig. 3.32—Diagonal sections of arc-cast molybdenum rods cut along slip planes after rupture at 2200°C in hydrogen (250X, etched)

Fig. 3.33 – Schematic of electro-optical extensometer tracker (Optron)

Fig. 3.34 – Optron and furnace for creep testing to 3000°C (Neg. P64-12-17E)

Fig. 3.35 – Electron-beam-welded tungsten wire targets used for the measurement of creep with the Optron (Neg. P64-12-38B)

TABLE 3.4
CREEP DATA FOR ARC-CAST MOLYBDENUM^a AT 1800°C AND 2200°C OBTAINED WITH THE OPTRON

Specimen No. for M(6) Material	Test Temperature, °C	Stress, kg/mm ²	Test Time, hr	Test Atmosphere	Room Temperature Elongation %	Elongation Per Optron, %	Optron Elongation Error, %	2.54 cm Gage Length Second Stage Creep Rate, min ⁻¹	Total Train Second Stage Creep Rate, min ⁻¹	$\epsilon - \epsilon_0 = bt^m$				Duration Of First Stage Creep, min.
										$\epsilon - \epsilon_0 = bt^m$				
										m				
										ϵ vs t^m	$\log(\epsilon - \epsilon_0)$ vs $\log t$	ϵ_0	b	
36	2200	0.32	4.28	Argon	51.8	(rupture)	-	1.0×10^{-3}	1.2×10^{-3}	b	b	b	b	13
17	2200	0.39	2.03	Argon	48.7	(rupture)	-	2.3×10^{-3}	2.6×10^{-3}	0.65	0.65	0.0005	0.0076	8
45 ^c	2200	0.32	0.88	Argon	6.20	6.96	+12.0	1.1×10^{-3}	-	0.65	0.60	0.0009	0.0049	18
1-3	2200	0.32	0.63	Argon	4.60	1.55	-1.0	9.9×10^{-4}	-	0.60	0.62	0.0008	0.0048	13
1-1	2200	0.32	0.62	Hydrogen	3.60	3.54	-1.7	7.5×10^{-4}	9.5×10^{-4}	0.65	0.65	0.0005	0.0030	12
44	2200	0.30	0.58	Hydrogen	d	2.60	-	5.2×10^{-4}	-	0.65	0.65	0.0013	0.0024	19
1-2	2200	0.32	0.63	Hydrogen	3.62	3.63	+0.3	7.8×10^{-4}	9.8×10^{-4}	0.65	0.64	0.0013	0.0030	13
2-1	2200	0.39	0.32	Hydrogen	4.83	4.75	-1.7	1.9×10^{-3}	2.8×10^{-3}	0.65	0.64	0.0028	0.0062	9
2-2	2200	0.20	1.20	Hydrogen	0.93	0.92	-5.0	Not run to second stage		0.80	0.80	0.00055	0.00028	>72
2-8	2200	0.25	4.75	Hydrogen	8.13	8.25	+0.9	2.5×10^{-4}	-	0.75	0.75	0.0017	0.0010	85
2-11	2000	0.70	0.77	Hydrogen	d	9.60	-	1.7×10^{-3}	-	0.60	0.57	0.0025	0.0069	8
2-9	2000	0.50	3.70	Hydrogen	9.50	9.11	-4.1	3.7×10^{-4}	4.8×10^{-4}	0.75	0.79	0.0014	0.0013	70
2-4	1800	1.20	0.65	Helium	8.42	8.40	+0.2	1.8×10^{-3}	2.6×10^{-3}	0.70	0.71	0.0030	0.0056	13
2-3	2000	0.32	20.83	Helium	9.55	9.70	-1.5	7.0×10^{-5}	8.3×10^{-5}	0.60	0.60	0.0000	0.000064	110

^aAll samples annealed for 2 hours at test temperature before test.

^bTracker unlocked on sample loading - sample removed, first stage data not obtained.

^cCyclic temperature control.

^dTarget wire broken when removing sample from furnace.

sufficiently identify the second stage of creep and then terminated. By terminating the tests prior to rupture, the strains determined by the Optron could be verified at room temperature using a micrometer slide comparator. Data are tabulated in Table 3.4, and, in general, show good agreement. In addition to the Optron data, elongations for the total load train were automatically obtained with a linear variable differential transformer (LVDT) for comparison purposes. Good agreement was obtained with earlier data for molybdenum, at the same conditions, when only the LVDT was used for elongation measurements. Typical creep curves obtained with the Optron are shown in Figures 3.36 and 3.37. The curve in Figure 3.36 shows the primary and secondary stages of creep recorded continuously from the time of load application. The curve in Figure 3.37 is a similar curve using an expanded scale for the initial phase of primary creep and demonstrates the potential for investigating in more detail the strain - time relationship in the very early stages of creep for materials to 3000°C.

First-stage creep data for arc-cast molybdenum, obtained with the Optron, were analyzed by a method similar to that proposed by Hazlett and Parker and discussed earlier in the section. The value of m was determined by trial and error until a plot of strain versus t^m , on rectangular coordinates yielded a straight line to the initiation of second-stage creep. The initiation of second-stage creep was determined from an expanded plot of the conventional creep curve on rectangular coordinates. The slope of the line gives b , and the intersection of the line at time zero, the intercept ϵ_0 . An example is shown in Figure 3.38a. The slope, intercept, and exponent were then used to reconstruct the curve and verify the values obtained. Excellent agreement is shown in Figure 3.38b between the calculated curve and the experimental data. As discussed earlier, the basic equation yields a straight line of slope m when $\epsilon - \epsilon_0$ versus t is plotted on logarithmic coordinates. Using the ϵ_0 determined above, such a plot is presented in Figure 3.38c yielding a slope (m) of 0.71. Good agreement is therefore obtained by the two techniques for the exponent value m in the primary creep equation. Table 3.4 lists the m values obtained by the two techniques for the tests of arc-cast molybdenum performed to date. Also included in Table 3.4 are the ϵ_0 and b values for each test.

COMMERCIAL W - 25Re SHEET

W - 25Re (at. %) sheet, 0.05 cm thick, purchased from all known vendors in 1964, is being evaluated. Six different lots of sheet material were received from four U. S. and one foreign producer. One vendor supplied both arc-cast and powder metallurgy sheet. Another vendor manufactured only arc-cast sheet with the remaining vendors producing powder metallurgy sheet. A letter detailing the objectives of this program was forwarded to each vendor when the material was ordered.

Quality of "As-Received" Commercial W - 25Re Sheet

The chemical composition of the purchased W - 25Re sheets, as reported by the vendors, is given in Table 3.5 which includes the impurity content (C, H₂, O₂, and N₂) as determined by GE-NMPO. Among the metallic impurities given in Table 3.5, the Mo, Fe, Nb, Cu, and Al values showed the largest variance between producers, but are not believed significant at this time. The non-metallic impurity analyses obtained by GE-NMPO were processed as a single group of carefully prepared analytical specimens, and are considered comparable. In some cases, considerable differences exist between the vendor and GE-NMPO analyses of these non-metallic constituents.

As a quality check before considering W - 25Re sheet for nuclear applications, simulated electron-beam welds on the sheet are radiographically evaluated for porosity or voids. In part, the voids are believed to form because of carbon monoxide gas release within the weld fused metal. Due to the vacuum during EB welding, no external contamination of

Fig. 3.36 - Creep curve for arc-cast molybdenum (Specimen M-6-44) at 2200°C and 0.30 kg/mm² stress in helium

Fig. 3.37 - Creep curve for arc-cast molybdenum (Specimen M6-2-4) at 1800°C and 1.20 kg/mm² stress in helium

GE-NMPO

Fig. 3.38 – Strain-time correlations for arc-cast molybdenum at 1800°C and 1.20 kg/mm² stress

TABLE 3.5
CHEMICAL COMPOSITION OF SIX LOTS OF PURCHASED W - 25Re SHEET

Element, wt %	EV-1		EV-2		EV-3		EV-4 ^a		EV-5 ^b		EV-7	
	(Arc-Cast)		(Power Metallurgy)		(Arc-Cast)		(Powder Metallurgy)		(Arc-Cast)		(Powder Metallurgy)	
	Vendor	GE-NMPO ^c	Vendor	GE-NMPO ^c	Vendor	GE-NMPO ^c	Vendor	GE-NMPO ^c	Vendor	GE-NMPO ^c	Vendor	GE-NMPO ^c
Re	24.5		-		25.48		25.0		-		24.93	
W	Bal		74.91		-		Bal		-		-	
Element, ppm												
C	40 - 70	22.0	-	32.0	15 ^d	20.0	40	22.0	40	33.0	10 - 11	31.0
N	-	0.4	-	0.5	9	0.4	5	2.2	13	1.0	1 - 2	0.1
O	<50	11.9	-	4.6	14	7.6	50	3.8	25	11.4	2 - 20	17.4
H	3.0 - 3.2	0.2	-	0.4	<1	0.6	1.9	0.2	4	0.3	2 - 3	0.5
Al	30		<1		<10		20		-		<10	
Nb	<100		ND ^e		-		50		-		-	
Cd	<5		-		-		1		-		-	
Co	30		-		<5		-		-		<1	
Cr	<20		-		<10		5		-		<10	
Cu	40		5		13		1.5		-		-	
Fe	<20		50		7		36		-		<10	
Mg	<20		<1		<11		1		-		<10	
Mn	<20		-		<10		2		-		<1	
Mo	250		<50		44		200		-		<10	
Ni	<20		3		2		15		-		<1	
Pb	<20		ND		<20		5		-		<1	
Si	<100		<1		-		35		-		<10	
Sn	<20		-		<20		10		-		<1	
Ti	<20		ND		<1		10		-		<1	
V	<20		-		<10		5		-		<1	

^aEV-6 as single piece-part lot on EV-4. Separate analysis was provided, and was similar to that shown for EV-4.

^bGiven by vendor as "typical analysis."

^cConductometric carbon analysis; gaseous elements by vacuum fusion method.

^dComposition given represents 226.8 g of sheet only. A larger sheet of 263.9 g was similar in composition except for 54 ppm carbon compared to 15 ppm as given above.

^eNot detectable.

the sheet is considered probable in this evaluation. During this report period, 5 cm of EB simulated welds were completed on test pieces selected from positions on the W - 25Re sheet adjacent to the chemical analysis specimens. The number of pores or voids in the EB weld fused areas are given in Table 3.6 in the order of increasing C + O₂ content of the sheet. Two conclusions may be derived from the results given in Table 3.6.

TABLE 3.6
VOIDS DETECTED RADIOGRAPHICALLY IN SIMULATED
ELECTRON-BEAM WELDS ON W - 25Re SHEET^a

Test Number	Analyses, ppm ^b				Sum Of Carbon And Oxygen	Number Of Voids Observed In 5-cm Weld Length
	C	O ₂	H ₂	N ₂		
EV-4	22.0	3.8	0.2	2.2	25.8	0
EV-3	20.0	7.6	0.6	0.4	27.6	0
EV-1	22.0	11.9	0.2	0.4	33.9	1
EV-2	32.0	4.6	0.4	0.5	36.6	8
EV-5	33.0	11.4	0.3	1.0	44.4	17
EV-7	31.0	17.4	0.5	0.1	48.5	Many

^aTwo 2.5-cm-long simulated electron beam welds. No contamination probable because of vacuum welding.

^bConductometric carbon analysis; gaseous elements by vacuum fusion method.

1. The number of voids increased with increasing carbon content; therefore, the carbon content should be as low as possible. By coincidence, the carbon levels given in Table 3.6 fall into two groups, 20 to 22 ppm and 31 to 32 ppm. The first group developed few voids in welding. Based on these and previously obtained data, GE-NMPO has specified a carbon range of 8 to 22 ppm with less than 15 ppm preferred in laboratory-produced "reference" W - 25Re sheet.
2. An oxygen content as low as possible is preferred in W - 25Re sheet. A relatively low oxygen content tends to react with high carbon content to develop voids in weld areas as shown for EV-2 in Table 3.6. Similarly, a high oxygen and low carbon content can cause void formation as shown for EV-1 in Table 3.6. The GE-NMPO current specification for "reference" material is less than 10 ppm O₂ with less than 6 ppm preferred.

Additional quality measurements completed for each W - 25Re sheet are as follows:

1. Thickness measurements were made at nine positions on each of the sheets supplied on each purchase.
2. Each sheet was photographed with oblique lighting to reveal surface texture.
3. Each sheet was radiographed to disclose defects, gage variations, and density irregularities.
4. Each sheet was scanned with an ultrasonic tester to indicate the presence of internal defects in the sheet.
5. Each sheet was given a dye penetrant test (Zyglo). This test is effective in detecting surface defects and sheet edge laminations due to improper edge preparation.

After completion of the above tests, defective areas were marked on the sheets, and the acceptable areas designated for bend and creep-rupture specimens as shown in Figures 3.39 through 3.44. The "as-received" test results are given in Table 3.7.

In general, the gage variations, edge laminations, general internal defects detected ultrasonically, and the quality shown by radiographic inspection indicate that a large percentage of each W - 25Re sheet surveyed failed to meet reasonable quality standards

AS-RECEIVED Showing surface texture

X-RAY

ULTRASONIC TRACE Showing internal defects

MARKED Showing areas of defects

Fig. 3.39 – Results of ultrasonic and X-ray inspection of W – 25Re sheet, sample EV-1

Fig. 3.40 – Results of ultrasonic and X-ray inspection of W – 25Re sheet, sample EV-2

Fig. 3.41 – Results of Ultrasonic and X-ray inspection of W – 25Re sheet, sample EV-3

AS-RECEIVED
Showing surface texture

X-RAY

ULTRASONIC TRACE

Showing internal defects

MARKED
Showing areas of defects

Fig. 3.42 – Results of ultrasonic and X-ray inspection of W-25Re sheet, sample EV-4

AS-RECEIVED Showing surface texture

X-RAY

ULTRASONIC TRACE Showing internal defects

MARKED Showing areas of defects

Fig. 3.43 – Results of ultrasonic and X-ray inspection of W-25Re sheet, sample EV-5

Fig. 3.44 – Results of ultrasonic and X-ray inspection of W – 25Re sheet, sample EV-7

TABLE 3.7
SUMMARY OF NON-DESTRUCTIVE TESTS ON COMMERCIAL W - 25Re

Assigned Lab No.	Sheet No.	Room Temperature Bend Ductility Transverse (4 x t radius)	Range In Thickness (Eight Measurements Per Sheet), cm	Comments On Meeting The 0.508 cm Ordered Thickness	Due To Gage, ^a GE-NMPO Applications Would:	Due To Surface ^b Texture, GE-NMPO Would:	Dye Penetrant Inspection	Based On Radiographic Analysis GE-NMPO Normally Would: ^c	Based On Ultrasonic Scanning Of Sheet For Sound Absorption GE-NMPO Normally Would: ^d	Rejected For High-Temperature Testing Program, ^e %
EV-1	1	90°	0.038 - 0.049	Thin	Reject	Reject	Few pits	Reject 15 - 100%	Reject 15% - ends	10
	1A		0.041 - 0.043	Thin	Reject	Reject	Pits	Reject 70 - 100%	Accept	10
	1B		0.043 - 0.048	Thin	Reject	Accept	End laminated	20% - edges to end reject	Reject 20% - ends	5
	1C		0.043 - 0.049	Thin	Reject	Accept	End laminated - pits	15% - edge to end reject	Reject 15% - ends	40
	1D		0.041 - 0.048	Thin	Reject	Accept	End laminated - 2 pits	10% (end) to 100% reject	Reject 20% - ends	20
EV-2	2		0.046 - 0.050	Within 10% of gage but overall thin	Reject	Accept	Pits - end laminated	30% reject - edges to corners	Reject 25% - edges	20
	2A		0.046 - 0.050		Reject	Accept	OK	30% reject - edges	Reject 20% - edges	25
	2B		0.046 - 0.052		Reject	Accept	Pit - edge lamination	Reject 100% - edges and density	Reject 40% - edges	40
	2C		0.047 - 0.050		Reject	Accept	Pits - edge lamination	Reject 30% - edges and end	Reject 40% - edges	20
EV-3	3		0.049 - 0.052	Good	Accept	Accept	All edges laminated	Density irregularities	Reject 75%	75
	3A		0.051 - 0.054	BL ^f - heavy	Reject	Accept	All edges laminated	and longitudinal grinding	Reject 75%	75
	3B		0.048 - 0.050	Large range	Reject	Accept	OK	of surface make all EV-3	Reject 25%	25
	3C		0.048 - 0.053	Large range	Reject	Accept	One edge laminated	sheets borderline	Reject 30% - edge	30
	3D		0.050 - 0.055	BL - heavy	Reject	Accept	OK		Reject 10% - end	10
EV-4	4		0.052 - 0.059	Large range - heavy	Reject	Borderline	Edge laminated	5% reject in 2 edge spots	Reject 66%	66
	4A		0.054 - 0.059	Heavy	Reject	Borderline	All edges laminated	OK	Reject 50%	50
(EV-6 is part of EV-4)	4B		0.042 - 0.047	Thin	Reject	Accept	OK	Reject 20% - density	Reject 30% - edge	30
	4C		0.050 - 0.057	Heavy	Reject	Reject	Edge laminated	OK	Reject 40%	40
	6		0.053 - 0.056	Heavy	Reject	Reject	End and edge laminated	Reject 25% - edges	Reject all	100
EV-5	5		0.049 - 0.053	Good	Accept	Reject	OK	Reject - ends, corners, general	Reject 25%	25
	5A		0.049 - 0.054	Good	Accept	Reject	Small pits	Reject - ends, corners, general	Reject 10% - corners	10
	5B		0.048 - 0.055	Large range	Reject	Reject	OK	Reject except ripples, general	Reject 75%	75
	5C		0.049 - 0.056	Large range	Reject	Reject	OK	Reject - ends and ripples	Reject 75%	60
	5D		0.049 - 0.054	Good	Accept	Reject	OK	Reject - one spot - general	Reject 80%	80
EV-7	7		0.049 - 0.052	Good	Accept	Accept	Edge laminated	Consider as 2 pieces	Reject 15% - edge	15
	7A		0.048 - 0.050	Light	Reject	Accept	OK	Consider as 2 pieces	Reject 5% - edges	0
	7B		0.045 - 0.052	Large range	Reject	Accept	Edge laminated	Consider as 2 pieces	Reject 60%	60
	7C		0.043 - 0.051	Large range	Reject	Accept	Edge laminated	Consider as 2 pieces	Reject 60%	60

^aAssumes high-stress application combined with the usual reactor requirement: of closely controlling the quantities of materials in the reactor core.

^bSurface variations are sufficient to influence weld reliability, and probably aerodynamics characteristics of these surfaces. See Figures 3.39 through 3.44.

^cPercentage rejected would depend on reliability required for the end application.

^dLaminated areas are considered unweldable because normal refractory-metal experience shows weld burn-through in these areas. General defect areas are also questionable as to reliability. See Figures 3.39 through 3.44.

^eAreas shown on Figures 3.39 through 3.44 were rejected on the basis that they were apparently questionable in quality, and particularly should not be considered applicable to the stressed region of a creep-rupture test specimen.

^fBorder line.

in the as-received condition. These data show that all W - 25Re sheet purchased in 1964 would be rejected. The estimated percentage of each sheet rejected for use in the high-temperature portion of this program is summarized by the last column of Table 3.7.

Elevated-Temperature Stability

Room-temperature bend tests were conducted on the representative commercial W - 25Re sheet after heating in hydrogen for 100 hours at temperatures from 1200°C to 2200°C, and for shorter periods at 2600°C and 3000°C. The bend-test results given in Table 3.8 were performed in accordance with Military Advisory Board recommendations for refractory-metal sheets. As shown in Table 3.8, W - 25Re bend-test specimens from arc-cast sheets EV-1 and EV-3 developed poor bend ductility when heated at 2200°C or higher and also developed very large grains when heated to 3000°C, as shown in Figure 3.45. In contrast, the four sheet materials made using powder metallurgy techniques maintained useful room-temperature ductility after heating at temperatures to 3000°C. As shown in Figure 3.45, the grain sizes of the powder metallurgy process sheet remained medium- to fine-grained over the temperature range to 3000°C.

TABLE 3.8
ROOM-TEMPERATURE BEND TESTS^a FOR COMMERCIAL W - 25Re SHEET
FOLLOWING PROLONGED HOLDING AT HIGH TEMPERATURES

Assigned Lab No.	Bend Ductility As- Received ^b	1200°C			1400°C			1600°C			1800°C			2200°C		2600°C		3000°C ^c
		2 hr	10 hr	100 hr	2 hr	10 hr	100 hr	2 hr	10 hr	100 hr	2 hr	10 hr	100 hr	10 hr	100 hr	2 hr	10 hr	30 min.
EV-1	>90°	>90°	>90°	>90°	>90°	<10°	<10°	<5°	0°	<5°	10°	0°	30°	0°	5°	5°	0°	0°
EV-2	>90°	>90°	>90°	>90°	>90°	80°	5°	45°	>90°	>90°	>90°	45°	>90°	30°	60°	30°	45°	30°
EV-3	>90°	>90°	>90°	>90°	>90°	15°	<5°	10°	30°	30°	30°	10°	30°	5°	10°	10°	10°	5°
EV-4	>90°	>90°	>90°	>90°	>90°	45°	<5°	30°	45°	30°	30°	30°	30°	20°	>30°	30°	15°	20°
EV-5	>90°	>90°	>90°	>90°	>90°	15°	15°	>90°	30°	10°	30°	30°	>30°	10°	>30°	>15°	-	10°
EV-7	>90°	>90°	>90°	>90°	>90°	0°	<5°	>90°	80°	>90°	80°	45°	>90°	45°	45°	60°	30°	45°

^aBend test specimens 1 cm by 3 cm were cut for bending transverse to the sheet rolling direction. Specimens were cut from the sheet by electro-discharge machining, and edges ground with -250 grit paper parallel to rolling direction. Specimens were held at the indicated temperatures in hydrogen atmospheres. Bending was conducted in a bend jig constructed for 0.0508 cm sheet to meet Military Advisory Board recommendations. The as-received material was bent using an electronically controlled punch velocity of 1 inch per minute which meets the MAB specification. Following the prolonged heating, bends were made with a punch speed of 0.05 inch per minute.

^bRoom temperature bends. Transverse to rolling direction. Bend radius 4 x thickness. Punch speed 1 inch per minute.

^cRoom temperature bends. Transverse to rolling direction. Bend radius 4 x thickness. Punch speed 0.05 inch per minute.

The bend tests obtained for Table 3.8 following heating to 3000°C represent sound material heated at a slow heating rate. In contrast, several square centimeters of each material rejected by X-ray and ultrasonics were rapidly heated to 3000°C. As shown in Figure 3.46, sheet EV-7 developed numerous blisters when rapidly treated to 3000°C. This result confirms the many voids observed in the simulated electron beam weld for EV-7 as given in Table 3.6. No voids were developed by the remaining sheet items in this test.

Ductility Versus Temperature - Recrystallized Commercial W - 25Re Sheet

The addition of rhenium to tungsten produces an alloy which is ductile at room temperature after heating in the recrystallization temperature range whereas unalloyed tungsten is usually brittle. Bends were completed at 200°, 150°, 75°, 20°, and minus 50°C on each commercial W - 25Re sheet after heating for 10 hours at 1800°C and 2600°C in hydrogen. Similar bends were completed at room temperature and -50°C on the as-received sheet. Bend test results are given in Table 3.9. The fold of the bend was transverse to the sheet rolling direction with tests conducted in a silicone oil bath held at temperature.

In the as-received and in the 1800°C and 2600°C treated conditions, the commercial powder metallurgy W - 25Re alloys developed useful ductility down to -50°C. A general

Fig. 3.45 – Commercial W – 25Re as-received and after room-temperature bend test following a 30-minute treatment in H₂ at 3000°C (Murakami etchant all figures)

Fig. 3.45 (Cont.) – Commercial W – 25Re as-received and after room-temperature bend test following a 30-minute treatment in H₂ at 3000°C
(Murakami etchant all figures)

Fig. 3.46 - W - 25Re specimen EV-7 after 30-minute treatment in H_2 at $3000^\circ C$. Blistering or voids developed on several square inches. The area shown was rejected through X-ray and ultrasonic inspection techniques (Neg. 65-3-26, 1.5X)

TABLE 3.9

DUCTILITY VERSUS TEMPERATURE OF COMMERCIAL W - 25Re AS DETERMINED BY BEND TESTS^a

Assigned Lab No.	Basic Process In Fabrication Sheet	W - 25Re Sheet Heated 10 Hr At 1800°C In H_2					W - 25Re Sheet Heated 10 Hr At 2600°C In H_2					W - 25Re Sheet As-Received	
		Temperature Of Bend Test					Temperature Of Bend Test					Temperature Of Bend Test	
		-50°C	20°C	75°C	150°C	200°C	-50°C	20°C	75°C	150°C	200°C	-50°C	20°C
EV-1	AC ^b	10°	0°	5°	10°	10°	15°	0°	<5°	10°	30°	>90°	>90°
EV-2	PM ^c	45°	45°	>90°	>90°	>90°	15°	45°	60°	45°	>90°	80°	>90°
EV-3	AC	10°	10°	>15°	30°	45°	10°	10°	0°	>15°	30°	90°	>90°
EV-4	PM	45°	30°	30°	>90°	>90°	10°	15°	>30°	>30°	90°	>90°	>90°
EV-5	PM	15°	30°	10°	>90°	>90°	10°	10°	10°	30°	30°	-	>90°
EV-7	PM	30°	45°	>90°	>90°	>90°	30°	30°	45°	>90°	>90°	45°	>90°

^aAll bends completed at a punch speed of 0.05 inch per minute. Bend punch and fixture in accordance with Military Advisory Board suggestions for tungsten sheet. Heated specimens immersed in heated silicone oil throughout test cycle, and -50°C tests conducted in acetone - dry ice mixture.

^bAC = Arc-cast starting material for sheet.

^cPM = Powder metallurgy sheet.

lowering of ductility for the $1800^\circ C$ and $2600^\circ C$ recrystallized specimens occurred as the bend-test temperature decreased below $200^\circ C$, but a complete ductility loss did not develop. The arc-cast material exhibited lower ductility values throughout this evaluation series.

Comments applicable at this time to the commercial W - 25Re evaluation are:

1. Of the 28 sheets (7.5 cm by 30 cm) received for this program, 16 sheets, representing all but one producer, had laminated ends or edges. The laminated edges are believed attributable to poor shearing or cutting practices.
2. All vendors reported high values for O_2 , H_2 , and N_2 impurities and three out of five reported high values for carbon. This may be due to the method of preparing the samples for chemical analysis.
3. Rolling practices appeared generally poor, only five of the 28 pieces of W - 25Re sheet fell within ± 10 percent of the thickness tolerance. In addition, 60 percent of the product of one producer and all of the product of another producer now would be rejected because of excessive surface ripple. All the product of one producer was of doubtful value because half of each sheet appeared thinner than the other half.

4. Two producers provided sheets with numerous small surface pits. Another polished the sheet lengthwise because of apparent surface defects, and consequently thinned the center portion of the sheet.
5. Following recrystallization at 1800°C and 2600°C, the powder-metallurgy product developed useful bend ductility down to -50°C. The product produced by arc-cast methods was generally low in ductility compared to the powder metallurgy sheet.

W-Re-Mo ALLOY DEVELOPMENT

Creep-rupture tests of W-Re-Mo alloys were performed at 1600°C. The alloys were fabricated by GE-NMPO using the powder metallurgy technique, rolled into 0.05-cm-thick sheet, and annealed at 1400°C. Chemical analyses of the materials after fabrication into sheets are given in Table 3.10. The results show the material to be of quite high purity with the alloying elements close to the nominal values desired.

Table 3.11 lists the results for tests of the alloys at 1600°C and a stress of 4.22 kg/mm² in hydrogen. All specimens were annealed for 2 hours at 1600°C in hydrogen prior to testing. The elongation measurements are values obtained using an optical extensometer sighting on DPH marks at each end of the 2.54 cm gage section. Figures 3.47, 3.48, and 3.49 are creep curves obtained for the alloys, showing the effect of varying the rhenium content.

The W - 26Re alloy has the greatest rupture life and is the most creep resistant, based on the secondary (linear) creep rate, of all the alloys tested. Additions of 10 and 20 percent molybdenum to W - 26Re decreased the rupture life significantly as well as the hardness after test (Table 3.11), but did not increase the ductility based on the total elongation at rupture. W - 29Re, being the hardest of all the alloys, both before and after test, exhibited the greatest ductility (54%) based on the total elongation after test. For the W-Re specimens, the rupture life and secondary creep resistance decreased with increasing amounts of rhenium (decreasing amounts of tungsten) while the ductility and hardness increased. The W - 28Re and W - 29Re specimens with zero and 10 percent molybdenum showed a significant first-stage creep, whereas all other specimens showed little or no first-stage creep. As a group, the W-Re specimens with 20 percent molybdenum and the W - 26Re with varying amounts of molybdenum exhibited little or no first-stage creep.

Based on the data in Table 3.11, the hardness increased as the rhenium content was increased (decreasing amounts of tungsten), with or without molybdenum, and the hardness decreased with increasing amounts of molybdenum (decreasing amounts of tungsten) for the same rhenium content. Based on the total elongation measurements at rupture, increasing rhenium content (decreasing tungsten content) increased the ductility with or without molybdenum, while increasing amounts of molybdenum (decreasing amounts of tungsten) with the same rhenium content decreased the ductility.

The W-Mo-Re alloys were also evaluated for room-temperature bend ductility after holding at temperatures in the 1200° to 2600°C range. The room temperature bend-test results for these alloys, together with previously reported values for other alloys, are given in Table 3.12. However, the older test data show slightly more ductility than the current bend-test results, and are believed to indicate that small processing changes could result in higher ductility for the alloys. Higher stress-relief temperatures in cold-reduction operations are the major process differences between the old and the current alloy fabrication procedures. The results may be summarized as follows:

1. After holding at 2600°C, the alloys with 10 and 20 atomic percent molybdenum were more ductile than the binary W-Re alloys.

TABLE 3.10
CHEMICAL ANALYSES OF POWDER METALLURGY W-Re-Mo^a ALLOYS AFTER FABRICATION INTO 0.05 cm SHEET

Alloy	Re, at. % ^b	Mo, at. % ^b	Parts Per Million													
			C ^c	N ^d	O	H	Si ^e	Al	Fe	Ti	Cu	Ni	Cr	Ca	Mg	Mo
W - 26Re	26.01	-	39	0.3	4.9	0.4	5 to 50	T	5 to 50	T	T	T	T	T	T	100 to 1000
W - 27Re	26.94	-	34	0.3	7.3	0.3	T ^f	T	5 to 50	T	T	T	T	ND ^g	ND	100 to 1000
W - 28Re	28.41	-	43	0.3	5.3	0.1	5 to 50	T	5 to 50	T	T	T	T	T	T	-
W - 29Re	29.15	-	37	7	15	0.9	T	T	5 to 50	T	T	T	5 to 50	T	ND	100 to 1000
W - 26Re - 10Mo	26.09	10.86	-	18	20	0.3	-	-	-	-	-	-	-	-	-	-
W - 27Re - 10Mo	26.97	10.68	73	10	8.1	0.6	5 to 50	T	5 to 50	T	T	T	T	ND	ND	-
W - 28Re - 10Mo	28.37	10.68	43	63	12	0.1	5 to 50	T	5 to 50	T	T	T	T	T	T	-
W - 29Re - 10Mo	29.30	10.53	42	6	12	0.1	5 to 50	T	5 to 50	T	T	T	T	ND	ND	-
W - 26Re - 20Mo	26.88	20.20	-	6	17	0.8	5 to 50	T	5 to 50	T	T	T	T	ND	T	-
W - 27Re - 20Mo	27.33	20.33	37	29	6.9	1	5 to 50	T	5 to 50	T	T	T	T	ND	ND	-
W - 28Re - 20Mo	28.55	20.03	36	0.7	25	0.5	5 to 50	T	5 to 50	T	T	T	T	ND	T	-
W - 29Re - 20Mo	29.17	20.33	50	2	42	3	5 to 50	T	5 to 50	T	T	T	T	T	T	-

^aAlloy compositions are in atomic percent.

^bWet chemical analysis.

^cConductometric analysis.

^dVacuum fusion analysis.

^eSemi-quantitative analysis.

^fT - Trace, <100 ppm.

^gND - Not detected; the following elements were analyzed for and not detected in each sample: V, Mn, Bi, Zr, Pb, Sn, Ag, Co, Sb, As, B, Zn, Ba, Sr, Cd, Na, K, Li, and Nb.

TABLE 3.11

CREEP-RUPTURE RESULTS^a FOR W-Re-Mo ALLOYS AT 1600°C AND 4.22 kg/mm² STRESS IN HYDROGEN^b

Composition ^c	Time To Indicated Elongation, hr							Elongation At Rupture, %	Linear Creep Rate, min ⁻¹	Hardness, DPH ^d	
	0.5%	1%	2%	3%	5%	10%	Rupture			Before	After
W - 26Re	1.7	4.2	9.2	13.5	21.5	35.8	45.4	15	3.9×10^{-5}	524	475
W - 27Re	0.8	2.0	4.9	7.7	13.3	24.5	39.6	21	5.9×10^{-5}	550	475
W - 28Re	0.2	0.5	1.6	2.7	5.5	13.3	36.8	40	1.0×10^{-4}	572	550
W - 29Re	0.1	0.2	0.6	1.2	2.5	6.4	26.3	54	2.1×10^{-4}	627	575
W - 26Re - 10Mo	1.9	4.0	7.7	10.6	-	-	16.4	6	4.0×10^{-5}	485	450
W - 27Re - 10Mo	1.7	3.2	6.4	9.6	15.5	24.7	28.7	14	5.2×10^{-5}	530	480
W - 28Re - 10Mo	0.4	1.0	2.5	4.1	7.5	14.8	25.1	28	1.0×10^{-4}	540	485
W - 29Re - 10Mo	0.05	0.2	0.6	1.0	2.2	5.8	16.4	29	2.3×10^{-4}	600	530
W - 26Re - 20Mo	1.9	3.5	6.1	7.8	10.1	-	12.2	9	4.7×10^{-5}	495	415
W - 27Re - 20Mo	1.4	2.7	5.0	7.1	10.0	13.5	14.5	16	5.8×10^{-5}	495	425
W - 28Re - 20Mo	1.1	2.2	4.3	6.4	9.7	14.7	17.0	13	7.4×10^{-5}	525	465
W - 29Re - 20Mo	0.5	1.3	2.8	4.3	7.0	11.9	17.2	21	1.1×10^{-4}	525	500

^a0.05-cm-thick sheet, 0.6 by 2.54 cm gage section.^bAnnealed 2 hours at 1600°C in hydrogen before test.^cAtomic percent.^d5-kg load. Fig. 3.47 - Creep curves for W-Re alloys at 1600°C and 4.22 kg/mm² in hydrogen

Fig. 3.48 - Creep curves for W-Re-10Mo alloys at 1600°C and 4.22 kg/mm² in hydrogen

Fig. 3.49 - Creep curves for W-Re-20Mo alloys at 1600°C and 4.22 kg/mm² in hydrogen

TABLE 3.12
ROOM-TEMPERATURE BEND TEST^a RESULTS FOR ALLOYS HELD IN HYDROGEN FOR 10 OR 100 HOURS
AT THE INDICATED TEMPERATURE

Nominal Composition, at. %	1200°C		1400°C		1600°C		1800°C	2000°C	2200°C	2400°C	2600°C
	10 hr	100 hr	10 hr	100 hr	10 hr	100 hr	10 hr	10 hr	10 hr	10 hr	10 hr
W - 25Re	>90°	>90°	>90°	60°	>90°	>90°	45°	-	45°	45°	45°
W - 26Re ^b	45°	>90°	70°	30°	30°	90°	>90°	>90°		75°	90°
W - 27Re ^b	45°	90°	45°	30°	10°	30°	>90°	>90°		>90°	80°
W - 28Re ^b	5°	30°	<5°	10°	<5°	30°	60°	>90°		>90°	-
W - 29Re ^b	5°	<5°	<5°	0°	0°	10°	45°	80°		>90°	45°
W - 30Re	--	70°	-	30°	-	30°	30°	-	90°	>90°	90°
W - 25Re - 10Mo	>90°	>90°	>90°	>90°	-	>90°	-	-	45°	60°	90°
W - 26Re - 10Mo ^b	>90°	>90°	90°	30°	70°	90°	90°	90°		90°	90°
W - 27Re - 10Mo ^b	90°	90°	60°	15°	70°	90°	90°	>90°		>90°	70°
W - 28Re - 10Mo ^b	45°	30°	45°	10°	45°	90°	>90°	90°		>90°	-
W - 29Re - 10Mo ^b	5°	5°	30°	5°	10°	45°	60°	90°		>90°	>90°
W - 30Re - 10Mo	>90°	>90°	>90°	45°	>90°	45°	>90°	>90°	>90°	>90°	>90°
W - 25Re - 20Mo	>90°	70°	>90°	>90°	-	>90°	>90°	-	45°	60°	>90°
W - 26Re - 20Mo ^b	>90°	>90°	60°	30°	45°	90°	80°	60°		90°	90°
W - 27Re - 20Mo ^b	>90°	>90°	90°	45°	80°	90°	>90°	60°		45°	>90°
W - 28Re - 20Mo ^b	45°	90°	60°	45°	60°	>90°	>90°	>90°		90°	>90°
W - 29Re - 20Mo ^b	30°	60°	45°	15°	30°	>90°	>90°	>90°		>90°	>90°
W - 30Re - 20Mo	>90°	>90°	>90°	45°	>90°	45°	>90°	>90°	>90°	>90°	>90°

^aBends were completed with a 4 x thickness radius, using a punch speed of 0.05 inch per minute.

Bend fixtures in accordance with Military Advisory Board recommendations.

^bNew data.

- Both the W-Re binary alloys and the molybdenum-containing alloys were ductile after holding in the 2000° to 2400°C temperature range.
- With 20 percent molybdenum present, the alloys were ductile after holding 100 hours at 1600°C with similar results for 26 to 28 percent rhenium alloys having 10 percent molybdenum present.
- Alloys of 26 and 27 percent rhenium, with or without molybdenum, were ductile after holding 100 hours at 1200°C.
- As anticipated, the alloys of 28 and 29 percent rhenium content hardened on holding in the 1200° to 1600°C temperature range due to sigma phase precipitation. The addition of 20 percent molybdenum to the 28 and 29 percent rhenium alloys increased the bend ductility in these alloys.

The bend-test specimens were examined metallographically for sigma phase precipitation following most of the bend tests and the observations are summarized in Table 3.13. Both the W-Re binary and W-Mo-Re ternary alloys were observed to contain sigma phase as an intergranular precipitant after holding for 100 hours at 1400°C. In contrast, a generally distributed spheroidal shape was observed for the sigma phase precipitated at other temperatures as shown on Table 3.13.

New Alloy Development

Ruthenium, when added to chromium, molybdenum, or tungsten, also shows the ductilizing effect associated with rhenium. Unfortunately, rhenium has poor nuclear characteristics, but ruthenium is considered acceptable for thermal reactors. An exploratory series of 13 chromium alloys as arc-melted 50-gram buttons were cold press-forged with 50 percent reduction in thickness and results are shown in Figure 3.50. The cold ductility of the arc-cast chromium alloy buttons was arbitrarily rated at 1 for the most ductile down to 5 and 6 for the powdered or brittle buttons shown in Figure 3.50.

TABLE 3.13
SIGMA PHASE PRECIPITATION^a IN W-Re AND W-Re-Mo ALLOYS
AS INFLUENCED BY HIGH TEMPERATURES

Nominal Composition, at. %	Time And Temperature				
	100 Hours At 1400°C	100 Hours At 1600°C	10 Hours At 1800°C	10 Hours At 2000°C	10 Hours At 2600°C
W - 26Re	2	2	2	1	0
W - 27Re	2 ^b	3	3	1	0
W - 28Re	4 ^b	4	4	1	0
W - 29Re	5 ^b	5	5	3	0
W - 26Re - 10Mo	0 ^c	0	0	0	0
W - 27Re - 10Mo	1 ^b	1	1	0	0
W - 28Re - 10Mo	2 ^b	3	2	0	0
W - 29Re - 10Mo	4 ^b	4	4	0	0
W - 26Re - 20Mo	0 ^c	0	0	0	0
W - 27Re - 20Mo	0 ^c	0	0	0	0
W - 28Re - 20Mo	1 ^b	1	1	0	0
W - 29Re - 20Mo	2 ^b	3	2	0	0

^aNumbers 0 through 5 indicate rating of second phase quantity as depicted in photomicrographs.

^bPrecipitate concentrated in grain boundaries, and at intersections of grain boundaries.

^cPrecipitate not observed, but broadening of grain boundaries noted.

Fig. 3.50 – Chromium-base alloys after 50 percent reduction by cold-pressing (Neg. P65-2-21)

This program had three objectives:

1. To determine if the ductility of chromium increased as an addition element to the metal increased the average electron-to-atom ratio of the alloy
2. To permit a preliminary estimation of whether ruthenium could be substituted for rhenium in Cr-Re alloys on an atom-for-atom basis, or whether the ductilizing effect was related to the average electron-to-atom concentration of the alloy
3. To ascertain whether the entropy of the body-centered cubic structure of the solvent chromium is markedly changed by alloying with the larger molybdenum atom. However, this substitution does not change the electron-to-atom ratio. Therefore, an initial evaluation is permitted of the influence of entropy changes on the ductility of the solvent body-centered cubic Cr + Mo alloys as ruthenium additions increase the average electron-to-atom ratio. In view of the above objectives, the alloys are arranged into groups in Table 3.14, which includes the nominal composition of the alloy, calculated average electron-to-atom ratio, and assigned ductility value.

The Cr-Re-Ru group of alloys given in Table 3.14 shows that 25Ru (at. %) exerts a stronger ductilizing effect than 25Re (at. %). This can be seen by comparing alloys 1 and 11. Also, as ruthenium is systematically reduced and rhenium content increased with a constant 25 atomic percent total, the ductility of the ternary chromium alloys is sometimes poorer than that of the binary Cr - 25Re (at. %) alloy. Ruthenium makes a larger electron contribution per atom than rhenium; therefore, the ductility increases as the electron-to-atom ratio increases rather than as the number of atoms increases. However, one reservation must be considered; i. e., the rhenium atom is larger than the ruthenium atom.

In the second group of alloys in Table 3.14, the ruthenium addition was decreased as molybdenum was added to the chromium matrix. The ductility observed, the ruthenium concentration, and the electron-to-atom ratio decreased consistently in the group.

TABLE 3.14
COMPOSITIONS, DUCTILITY RATING, AND AVERAGE ELECTRON-
TO-ATOM RATIO OF CHROMIUM ALLOYS

Alloy	Nominal Composition, at. %				Ductility ^a After	Average
	Cr	Ru	Re	Mo	50 Percent Cold Press Reduction	Electron-To-Atom Ratio
Cr-Re-Ru Group						
1	75	25	-	-	1	6.50
7	75	20	5	-	2	6.45
8	75	15	10	-	3.0	6.40
9	75	10	15	-	3.5	6.35
10	75	5	20	--	3.5	6.30
11	75	-	25	-	3	6.25
12	70	10	20	-	3	6.50
13	80	20	-	-	3	6.40
Cr-Mo-Ru Group						
1	75	25	-	-	1	6.50
2	75	20	-	5	2	6.40
3	75	15	-	10	4	6.30
4	75	10	-	15	3	6.20
5	75	5	-	20	5	6.10
6	75	-	-	25	6	6.00

^aArbitrarily assigned rating with 1 the best rating down to 5 and 6 as alloys produced by 50 percent cold-reduction on a press-forged at room temperature.

Therefore, molybdenum additions to chromium did not influence the ductility of the body-centered cubic matrix. Introduction of molybdenum does not tend to influence the atomic structure or the electron-to-atom ratio of the alloy, but does introduce entropy effects through alloy mixing. Had a marked irregularity in the ductility sequence been observed in this series, a marked entropy effect would have been defined. However, the ductility of the body-centered cubic chromium matrix alloy appeared to be influenced only by ruthenium as the ductilizing addition alloy.

WORK PLANNED FOR NEXT PERIOD

Analysis of first-stage creep will be continued to evaluate the various correlations over a broader temperature range for arc-cast tungsten as well as other materials.

Creep-rupture evaluations of W-Re-Mo alloys will be performed at 2200°C for comparison to results obtained at 1600°C.

Creep-rupture tests of W - 25Re sheet obtained from six vendor sources will be initiated. Wrought powder metallurgy and arc-cast material will be included. Tests are planned at 1200°, 1600°, 2000°, and 2400°C for rupture times from 1 to 100 hours.

Purification techniques developed for W - 25Re will be evaluated for influence on the ductility of unalloyed molybdenum and low-rhenium-content molybdenum alloys.

Sixteen chromium-based alloys are being processed to confirm and extend the ductility increase obtained by increasing the electron-to-atom ratio in the alloy by ruthenium additions. In addition to Ru, the new alloys will include Fe, Co, Ni, Re, and Os as additions to chromium.

A major effort is underway to develop processing procedures for seamless tubing of W - 25Re - 30Mo alloy by the close of FY-1965.

4. EFFECT OF RADIATION ON HIGH-TEMPERATURE METALS AND ALLOYS

(57004)

The objective of this program is to determine the effect of radiation on the time-, temperature-, and stress-dependent properties of selected high-temperature alloys and refractory metals, to identify the causes of any observed changes in these properties, and to develop remedial measures.

The radiation effects studies are divided into two separate materials categories. The first considers a family of refractory metals and alloys, and the second, designated as the heat resistant metals and alloys program, includes the materials A-286, Hastelloy X, Hastelloy N, Fe-Cr-Al-Y alloys, and Type 304 stainless steel.

REFRACTORY-METALS AND ALLOYS PROGRAM

The experimental program to study the effects of neutron irradiation on the creep-rupture, tensile, resistivity, and hardness properties of refractory metals and alloys is continuing. In addition to studies on the above properties, theoretical calculations on the nature of the neutron-induced defects and the direct observations of defects by the use of the transmission electron microscope are being performed.

Some work on the determination of the true creep rate of tungsten, resistivity recovery studies of irradiated tungsten in the temperature region of $0.31 T_m^1$, and the hot-hardness of irradiated molybdenum, are discussed. A summary of the experimental program, test conditions, and preliminary results is presented in Table 4.1.

Status of Irradiations

The new series of test specimens (capsules ORM-31 through ORM-37) for use in the determination of the influence of neutron dose on the creep-rupture, tensile, and resistivity properties of tungsten are progressing according to schedule. The fast neutron values of this series of tests will range from about 1×10^{18} nvt up to approximately 3×10^{20} nvt.

Capsules ORM-31 through ORM-34 were returned from ORNL and disassembled. The new capsule design permitted the specimens to be removed in the hot cell with relative ease. Only one subminiature tensile specimen of the 32 specimens in the four capsules was accidentally damaged in disassembly. All specimens appeared to be in excellent condition with no trace of surface film.

The ORM-31 capsule was inadvertently positioned in the ORR-A2 hole so that the peak flux was not at the middle of the length of the capsule. This capsule did not, therefore, receive the original planned neutron dosage. The evaluation of the dosage will have to await the dosimeter results and a review of the dosimeter wire-probe flux plots recently

¹ T_m is the absolute melting temperature of the metal.

TABLE 4.1
SUMMARY OF MAJOR EXPERIMENTS IN THE REFRACTORY METALS AND ALLOYS RADIATION EFFECTS PROGRAM

Exp. No.	Objective	Property	Test Specimen		Irradiation Conditions ^c			Post-Irradiation Heat Treatment ^d		Test Conditions	Percent Change In Property ^d			Comments		
			Material ^a	Type	Lot Number ^b	Capsule Number	Temp, °C	nvt, neutrons/cm ² Thermal (E _n ≥ 1 Mev)	Temp, °C		Time, hr	Creep rate	Rupture life		Elongation	
1	To investigate the effects of neutron irradiation on the creep-rupture and tensile properties. To perform supporting studies on the effects of neutron irradiation on the hardness and resistivity properties.	Creep rupture	W	Rod	MK137(PM)-X	ORM-4	70	2.2 × 10 ¹⁸	5.8 × 10 ¹⁷		T, °C	σ(kg/mm ²)				
					MK137(PM)-X	ORM-8	70	9.5 × 10 ¹⁸	2.5 × 10 ¹⁸	1100	19.34	-10.0	15	-1		
					MK137(PM)-Y	ORM-6	70	2.0 × 10 ¹⁹	3.7 × 10 ¹⁸	1100	20.35	-40.0	74	-1		
					MK137(PM)-Y	ORM-8	70	9.5 × 10 ¹⁸	2.5 × 10 ¹⁸	1100	20.35	-	17	-		
					MK137(PM)-E	ORM-17	70	7.5 × 10 ¹⁹	1.6 × 10 ¹⁹	1100	20.35	-60	160	-7		
					MK137(PM)-E	ORM-19	70	3.9 × 10 ²⁰	8.2 × 10 ¹⁹	1100	18.28	-16	28	-10		
					MK137(PM)-Y	ORM-6	70	2.0 × 10 ¹⁹	3.7 × 10 ¹⁸	1100	18.28	-76	490	-6		
					MK137(PM)-Y	ORM-8	70	9.5 × 10 ¹⁸	2.5 × 10 ¹⁸	1400	13.01	-	1	10		
					MK137(PM)-J	ORM-19	70	3.9 × 10 ²⁰	8.2 × 10 ¹⁹	1400	10.55	-6	38	19		
					MK137(PM)-J	ORM-19	70	3.9 × 10 ²⁰	8.2 × 10 ¹⁹	1500	8.44	-8	10	-29		
					MK137(PM)-E	ORM-19	70	3.9 × 10 ²⁰	8.2 × 10 ¹⁹	1700	5.92	-13	9	-28		
					MK137(PM)-J	33MT-137	1300	2.2 × 10 ²⁰	1.8 × 10 ²⁰	900						
					W - 25Re	Sheet	PF(PM)	ORM-17	70	7.5 × 10 ¹⁸	1.6 × 10 ¹⁸	900	22.34	-76	280	-26
							RWS9(TM)-4	ORM-12	70	9.1 × 10 ¹⁹	3.2 × 10 ¹⁹	100	37.28	-30	60	8
							KDM-515A(AC)-8	ORM-20	70	3.5 × 10 ²⁰	8.0 × 10 ¹⁹	100	43.9	-52	55	-56
			KDM-515A(AC)-2	ORM-23			70	5.2 × 10 ¹⁹	1.4 × 10 ¹⁹	580	21.09	29	-96	-4		
			KDM-515A(AC)-1	ORM-13			70	5.5 × 10 ¹⁹	6.9 × 10 ¹⁸	980	10.55	-2	10	14		
			KDM-515A(AC)-1	ORM-16			70	1.4 × 10 ²⁰	3.7 × 10 ¹⁹	580	21.09	210	-65	-		
			50Mo-50Re	ORM-16			70	1.4 × 10 ²⁰	3.7 × 10 ¹⁹	600	21.09	57	-32	-		
			Ta	ORM-20			70	3.5 × 10 ²⁰	8.0 × 10 ¹⁹							
			Ta - 10W	Sheet	ORM-23	70	5.2 × 10 ¹⁹	1.4 × 10 ¹⁹								
					ORM-23	70	5.2 × 10 ¹⁹	1.4 × 10 ¹⁹								
			Tensile	W	Rod	MK142(PM)-G	33MT-138	70	3.6 × 10 ²⁰	1.3 × 10 ²⁰		371		Yield Strength (Brittle fracture)	Tensile Strength	Elongation
		MK142(PM)-B				ORM-9	70	2.8 × 10 ¹⁹	5.1 × 10 ¹⁸							
		MK142(PM)-C				ORM-10	70	9.3 × 10 ¹⁹	1.7 × 10 ¹⁹							
		Resistivity	W	Rod	MK142(PM)-E	ORM-7	70	2.5 × 10 ¹⁸	5.3 × 10 ¹⁸		-96		Resistivity			Warm-worked.
					MK142(PM)-D	ORM-11	70	1.2 × 10 ²⁰	3.3 × 10 ¹⁹		-96		105			
					MK142(PM)-F	33MT-113	1300	2.2 × 10 ²⁰	8.0 × 10 ¹⁹		-96		315			
					RWW5(PM)-A	ORM-14	70	6.2 × 10 ¹⁹	1.2 × 10 ¹⁹		-96		39			
					RWW5(PM)-C	33MT-113	1300	2.2 × 10 ²⁰	8.0 × 10 ¹⁹		-96		10			
					GEH(PM)-B	ORM-14	70	6.2 × 10 ¹⁹	1.2 × 10 ¹⁹		-96		15			
			W - 25Re	Rod	GEH(PM)-C	ORM-14	70	6.2 × 10 ¹⁹	1.2 × 10 ¹⁹		-96		80			
					GEH(PM)-L	33MT-113	700	2.2 × 10 ²⁰	8.0 × 10 ¹⁹		-96		118			
					ZM8003(AC)-5	ORM-18	70	1.1 × 10 ²⁰	3.7 × 10 ¹⁹		-96		2			
			Mo-TZM	Rod	ZM8003(AC)-5	33MT-113	700	2.2 × 10 ²⁰	8.0 × 10 ¹⁹		-96		74			
											-96		7			
											-96					
		Hardness	W	Sheet	411-1	ORM-15	70	1.3 × 10 ²⁰	3.5 × 10 ¹⁹		15	500 grams	DPH Hardness			Single crystal. From isochronal annealing studies. Polycrystal. From isochronal annealing studies.
											650		8			
		Mo	Sheet	KDM-515A(AC)-M(10)	ORM-30	70	9.2 × 10 ¹⁹	2.6 × 10 ¹⁹		1300		60				
										15	500 grams	5				
										300		18				
										1200		55				

TABLE 4.1 (Cont.)
SUMMARY OF MAJOR EXPERIMENTS IN THE REFRACTORY METALS AND ALLOYS RADIATION EFFECTS PROGRAM

Exp. No.	Objective	Property	Test Specimen			Irradiation Conditions ^c			Post-Irradiation Heat Treatment		Test Conditions	Percent Change in Property ^d			Comments					
			Material ^a	Type	Lot Number ^b	Capsule Number	Temp, °C	n_{VT} , neutrons/cm ² Thermal ($E_n \geq 1$ Mev)	Temp, °C	Time, hr		Creep rate	Rupture life	Elongation						
2	To determine the influence of post-irradiation heat treatment on the creep-rupture and tensile properties. To perform supporting post-irradiation annealing studies on the resistivity and hardness properties and to make direct observations on the sub-structure.	Creep rupture	W	Rod	MK137(PM)-Y	ORM-6	70	2.0×10^{19}	3.7×10^{18}	1100	1	T, °C	σ (kg/mm ²)	Creep rate	Rupture life	Elongation	Warm-worked.			
					MK137(PM)-Y	ORM-6	70	2.0×10^{19}	3.7×10^{18}	1400	1	1100	20.35	- 27	13	4				
					MK137(PM)-Y	ORM-8	70	9.5×10^{19}	2.5×10^{19}	1400	1	1100	20.35	- 73	190	-				
					MK137(PM)-E	ORM-19	70	3.9×10^{20}	8.2×10^{19}	1400	1	1100	18.28	- 64	210	- 6				
					MK137(PM)-J	ORM-17	70	7.5×10^{19}	1.6×10^{19}	1050	1	900	22.64	- 74	520	-10				
					MK137(PM)-J	ORM-17	70	7.5×10^{19}	1.6×10^{19}	1200	1	900	22.64	- 91	900	-17				
					MK137(PM)-J	ORM-17	70	7.5×10^{19}	1.6×10^{19}	1300	1	900	22.64	- 61	190	- 7				
					MK137(PM)-J	ORM-17	70	7.5×10^{19}	1.6×10^{19}	1400	1	900	22.64	- 56	160	-				
					MK137(PM)-J	ORM-17	70	7.5×10^{19}	1.6×10^{19}	1700	1	900	22.64	- 46	90	- 7				
					MK137(PM)-M	ORM-19	70	3.9×10^{20}	8.2×10^{19}	1700	43	900		- 80	710	4				
					MK137(PM)-M	ORM-19	70	3.9×10^{20}	8.2×10^{19}	1700	1	900		- 98	-	-				
					PF(PM)	ORM-12	70	1.5×10^{20}	3.2×10^{19}	1100	3	1100	37.26	- 39	51.9	- 4				
					W - 25Re Mo	Sheet	KDM-515A(AC)	ORM-23	70	5.2×10^{19}	1.4×10^{19}	757	8	580	21.09	- 27		62.0	-20.8	
								ORM-23	70	5.2×10^{19}	1.4×10^{19}	779	8	580	21.09	- 28		-	-	
				Tensile																
					W	Rod	MK142(PM)-B	ORM-9	70	2.5×10^{19}	5.1×10^{18}					Yield Strength	Tensile Strength	Elongation	To be tested.	
							MK142(PM)-C	ORM-10	70	9.3×10^{19}	1.7×10^{19}									To be tested.
				Resistivity																
					W	Rod	MK142(PM)-D	ORM-7	70	2.5×10^{19}	5.3×10^{18}	650	1	-196		Resistivity				
							MK142(PM)-D	ORM-14	70	6.2×10^{19}	1.2×10^{19}	650	1	-196		6				
							MK142(PM)-D	ORM-11	70	1.2×10^{20}	3.3×10^{19}	650	1	-196		12				
							MK142(PM)-E	ORM-11	70	1.2×10^{20}	3.3×10^{19}	1900	1	-196		72				
							W - 25Re Mo	Rod	RWW5(PM)-A	ORM-14	70	6.2×10^{19}	1.2×10^{18}	550	1	-196		1		
									GEH(PM)-B	ORM-14	70	6.2×10^{19}	1.2×10^{16}	450	1	-196		14		
				Hardness																
					W	Sheet	411-1	ORM-15	70	1.3×10^{20}	3.5×10^{18}	650	1	Load 650 500 grams		DPH Hardness			Single crystal.	
			KDM-515A(AC)-M(10)	ORM-30			70	9.2×10^{19}	2.6×10^{19}	300 1200	1	300 500 grams 1200		60 5 55 0			Polycrystal.			
3	To investigate the influence of specimen configuration, purity level, structure and substructure on the post-irradiation creep-rupture and tensile properties. To perform supporting studies on the post-irradiation resistivity and hardness properties.	Creep-rupture	W	Mo													To be irradiated.			
																	To be irradiated.			
		Tensile	W	Mo													To be irradiated.			
																	To be irradiated.			
		Hardness	W	Mo														To be irradiated.		
4	To determine the in-reactor creep properties of refractory metals and alloys.		W														In planning stage. Test conditions to be established when more data from experiments No. 1 and 2 are evaluated.			

made in this facility. A summary of these irradiations is presented in Table 4.2. Capsule ORM-35 is presently in the reactor, and capsules ORM-36 and ORM-37 are at Oak Ridge awaiting insertion. Capsule ORM-37 is similar to the ORM-31 through ORM-36 capsules, except that cadmium jackets were put on the specimens in order to lower the ratio of thermal neutrons to fast neutrons by a factor of approximately 4.

TABLE 4.2
IRRADIATION DATA FOR REFRACTORY-METAL CAPSULES

Capsule	Test Specimens		Quantity	Facility	Irradiation Conditions ^a		
	Material	Type ^b			Exposure, hr	Dosage, n/cm ² Thermal	(E _n ≥ 1 Mev)
ORM-31	W	CR(R)	4	ORR-A2	400	c	c
	W	H-R	2				
	W	T	2				
ORM-32	W	CR(R)	4	ORR-A2	20	5.8 x 10 ^{18d}	2.9 x 10 ^{18d}
	W	H-R	2				
	W	T	2				
ORM-33	W	CR(R)	4	ORR-A2	80	2.3 x 10 ^{19d}	1.2 x 10 ^{19d}
	W	H-R	2				
	W	T	2				
ORM-34	W	CR(R)	4	ORR-A2	480	1.4 x 10 ^{20d}	6.9 x 10 ^{19d}
	W	H-R	2				
	W	T	2				
ORM-35	W	CR(R)	4	ORR-A2 (Being irradiated)		3.0 x 10 ^{20e}	1.5 x 10 ^{20e}
	W	H-R	2				
	W	T	2				
ORM-36	W	CR(R)	4	ORR (Awaiting insertion)		6.0 x 10 ^{20e}	3.0 x 10 ^{20e}
	W	H-R	2				
	W	T	2				
ORM-37 ^f	W	CR(R)	4	ORR (Awaiting insertion)		~4 x 10 ^{19e}	6.9 x 10 ^{19e}
	W	H-R	2				
	W	T	2				
ORM-38	Mo	CR(F)	16	ORR-F2 (Awaiting fabrication)		3.0 x 10 ^{20e}	5.4 x 10 ^{19e}
	Mo	H-R	6				
	W	H-R	9				
	W	T	15				

^aAll irradiations at reactor ambient temperature.

^bCoded as follows: CR = creep-rupture specimen

(R) = round specimen

(F) = flat type

H-R = hardness and resistivity

T = tensile specimen

^cCapsule inadvertently positioned slightly above reactor midplane. Estimation of dosage cannot be made until dosimeters are processed and data evaluated.

^dEstimated dosage.

^eRequested dosage.

^fSpecimens are shielded by a cadmium jacket.

A new capsule, designated ORM-38, is scheduled for insertion in the ORR-F2 facility. It will be fabricated and sent to Oak Ridge early in the next reporting period. This capsule will contain three stages of specimens; each stage will contain a single type of specimen, either flat creep-rupture, resistivity, or tensile. A number of the resistivity specimens will possess integral electrical leads for emf measurements and for the current leads. These resistivity specimens will be used for post-irradiation annealing studies at elevated temperatures following irradiations at fast neutron doses greater than approximately 5×10^{19} nvt.

Tungsten Creep-Rupture Tests

Two methods were used in obtaining elongation (creep) values on control and irradiated refractory metals and alloys. One method of measurement employs a linear variable differential transformer (LVDT) and a recorder; the other employs a dial gage indicator. Both methods measure the total deformation produced in the specimen and load train. The data met the requirements, on a relative basis, for the comparisons of creep rates between control and irradiated specimens. The true creep rate, however, is required for the interpretation of the influence of neutron irradiation on the effective activation energy for creep of the body-centered cubic (BCC) metals.

A study was therefore initiated to determine the true creep rate occurring across the test specimen gage section. The investigation involved the determination of two corrections; one necessitated by total load train relaxation, and the other, by axial temperature gradient. Results from the total load train effects only will be reported here. Future evaluations will include the correction for the combined effects.

The measurement technique was based on the use of an optical extensometer consisting of paired filar micrometer telescopes sighted on diamond pyramid hardness (DPH) indents placed on the test specimen gage section. This technique is consistent with a method reported previously,² except that round specimens are used.

A strain versus time plot for the case of one tungsten creep test at a temperature of 1100°C and a stress of 16.17 kg/mm² in hydrogen is shown in Figure 4.1. The plot shows a comparison of the results obtained with both the LVDT and the optical extensometer. As shown in the figure, the dial gage indicator results are very close to those obtained with the LVDT unit. The optical extensometer strain value shown was measured over an effective gage length of 2.54 cm. The LVDT measurements were taken on the load train external to the furnace, and the strain calculated on the actual specimen gage length of 4.45 cm. During the early stages of the tests, the load train (LVDT) strains were greater than the strains measured across the 2.54 cm center portion of the gage length (optical measurements). However, when the load train assembly reached steady state motion, the optically measured strain was greater (~13%) than that indicated by the LVDT system. Since this apparent crossover occurred before any significant necking-down of the specimen, the greater strain rate is believed to be caused mainly by the slightly higher temperature profile existing across the center portion of the specimen gage length.

The test specimens contained a number of DPH indents axially positioned along the gage section. Pre- and post-test room temperature length measurements were taken between indents to determine incremental strains as a function of gage position. These will be correlated with temperature-gradient studies in an attempt to derive strain corrections.

Resistivity Tests

It was previously reported³ that, in addition to the several relatively low temperature recovery regions, a resistivity recovery peak in irradiated tungsten occurs at approximately 860°C (0.31 T_m), and the radiation-induced mechanical property increments appear to anneal out at 0.35 T_m . These two recovery peaks are probably closely related and controlled by the same mechanism. In view of the importance of determining the recovery kinetics of this mechanism, a rather concentrated effort was undertaken to study the isothermal resistivity recovery near 0.31 T_m of tungsten specimens irradiated at reactor ambient temperature to several different fast neutron doses.

²"Fourth Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume I - Materials," GE-NMPO, GEMP-334A, February 26, 1965, pp. 22-23.

³J. Moteff and J. P. Smith, "Recovery of Defects in Neutron Irradiated Tungsten," ASTM Symposium on Flow and Fracture Behavior of Metals and Alloys in Nuclear Environments, June 22-24, 1964. (To be published in ASTM Proceedings of the meeting.)

Fig. 4.1 – Comparison of strain measured across the center 2.54 cm of gage section determined by the twin-scope optical extensometer with the apparent strain across the total gage section (4.45 cm) determined from the total load-train movement

Isothermal Resistivity Recovery Measurements At -196°C - Thermal treatment in argon for this series of experiments involved inserting a tungsten boat containing the specimens (0.3-cm-diameter rod) into an Inconel muffle within a wire-wound furnace which was heated to the preselected temperature. In addition to heat treating the irradiated samples, as a general rule, two unirradiated control samples of the same material were also heat treated at the same time. Although this method of heating is not the most rapid method for obtaining the desired temperatures, other more rapid techniques which were tried require further development. A correction factor was used to correct the data for the transient time required to reach the desired temperature. This correction factor was determined by monitoring the temperature of an instrumented tungsten sample as a function of time following insertion into the furnace. Then, by determining the area under the curve, defined by equation (4.1), plotted as a function of time,

$$F(\Delta H, T_0, T, t) = \theta/t = \frac{e^{-\Delta H/kT}}{e^{-\Delta H/kT_0}} \quad (4.1)$$

the temperature-compensated time (θ) may be determined where

ΔH = activation energy for the migration of some defect

k = Boltzman constant

T = temperature at time, t

T_0 = desired test temperature

t = time

θ = temperature-compensated time.

Since it is presently felt that the recovery near $0.31 T_m$ is possibly caused by vacancy migration, or the dissociation of vacancy clusters and/or vacancy-impurity atom complexes, the activation energy for this process is probably near 3 ev. Typical plots of the function given in equation (4.1) for $\Delta H = 2, 3$, and 4 ev, and a desired test temperature (T_0) of 757°C are shown in Figure 4.2. The temperature-compensated times are listed in the insert of the figure. As indicated, errors in the time correction for the assumed activation energies are very small, especially when considering annealing times of 15 minutes (900 seconds) or greater. Later studies will include annealing times which are less than 15 minutes.

Fig. 4.2—Temperature-compensated time correction factor as a function of time for several assumed activation energies for defect migration

Isothermal recovery of the resistivity (measured at -196°C) for two different neutron irradiation doses (1.3 and 3.3×10^{19} nvt, $E_n \geq 1$ Mev) are shown in Figures 4.3 and 4.4. For the case of samples irradiated to the low dose in ORM-14 capsule (Figure 4.3), a new specimen was added whenever the temperature was changed to determine if the recovery was controlled by prior post-irradiation heat treatment. The recovery at $0.31 T_m$ does not appear to be controlled by the initial defect concentration, which is in agreement with the results shown at the lower recovery peak ($0.15 T_m$) for tungsten.³ One specimen from the higher dose irradiation capsule (Figure 4.4) continued to show recovery after 100 hours of annealing at a temperature of 858°C . This indicates that the radiation-induced defect configurations are still changing in some manner and have not yet reached some equilibrium value, as those specimens which were irradiated to the lower dose.

Analysis of all the above results is now underway to determine reaction order and activation energy for the radiation-induced defect recovery. This information, coupled with other phases of the experimental program on the BCC metals, should yield valuable information into radiation damage and recovery mechanisms.

Elevated Temperature Resistivity Measurements - A program was initiated to measure the resistivity at the annealing temperature, instead of obtaining the values at liquid nitrogen temperatures (-196°C). For the initial measurements, unirradiated tungsten wires

³Ibid.

Fig. 4.3—Isothermal resistivity recovery of recrystallized tungsten irradiated in ORM-14 (1.3×10^{19} nvt, $E_n \geq 1$ Mev) at 779.5°, 820°, and 858°C

Fig. 4.4—Isothermal resistivity recovery of recrystallized tungsten irradiated in ORM-11 (3.3×10^{19} nvt, $E_n \geq 1$ Mev) at 779.5°, 820°, and 858°C

(0.1 cm in diameter) were used. The test apparatus and equipment are similar to those conventionally used; the major difference is that thin lead wires spot welded to the test specimen are used for the emf measurements rather than the pressure-type knife-edge contacts used previously. The emf leads are made of 0.02-cm tungsten wire. The current leads are much larger in diameter and are made of molybdenum or platinum, the latter being preferable because of ease of welding. Since the tungsten-wire to tungsten-rod welds are very brittle, a fairly rigid support structure is required for the test assembly. The support fixture is made with standard high-purity, high-density Al_2O_3 thermocouple protection-tube material which also may be used as the lead wire insulation. Measurements were obtained on two unirradiated specimens at temperatures up to 1130°C . As shown in Figure 4.5, the reproducibility of measurements on heating and cooling appears to be good. No induced emf originating from the furnace windings was observed nor was there any apparent thermocouple effect. Higher test temperatures were not possible because of the Inconel muffle material operating temperature limitations.

Hardness Tests

Hardness testing is continuing on the irradiated BCC metals. A series of experiments were initiated in which the hot-hardness values of unirradiated, irradiated, and worked molybdenum specimens will be compared. Since the tests on the worked molybdenum specimens were recently started, results will not be discussed at this time.

Fig. 4.5 – Resistivity of as-received (stress-relieved) tungsten wire

Hot-hardness testing of irradiated molybdenum specimens shows results similar to those obtained previously on tungsten single crystals. Figure 4.6 shows a plot of hot-hardness as a function of test temperature for both a control and an irradiated ($\sim 2.6 \times 10^{19}$ nvt, $E_n \geq 1$ Mev) specimen. For the case of irradiated molybdenum, the irradiation-induced hardness increment (65%) at 150°C is much greater than that (20%) observed at room temperature. These results are consistent with those observed⁴ for the case of irradiated tungsten in that the hardness is affected much more above than below a temperature of approximately $0.15 T_m$.

Fig. 4.6 - Hardness of irradiated and unirradiated polycrystalline molybdenum as a function of temperature

The effect of annealing on the room-temperature and elevated-temperature hardness of the irradiated specimens was determined in the following manner. Hardness indentations were made at room temperature and then at an elevated temperature, e. g., 300°C. The specimen temperature was then increased to the desired annealing temperature, e. g., 750°C, and held for 1 hour prior to making three indents. The specimen temperature was

⁴"Fourth Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume I - Materials," GE-NMPO, GEMP-334A, February 26, 1965, Figure 2.26, p. 80.

then reduced to 300°C and a series of three indents made after holding at temperature for 15 minutes. Following the 300°C indentation, the specimen temperature was reduced to ambient values. Indents were then made at room temperature after which the sequence was repeated at the next higher annealing temperature. In this manner, the room-temperature, 300°C temperature, and the various elevated-temperature hardness values were obtained following the 1-hour anneals at each temperature.

The results of the room-temperature hardness values are presented in Figure 4.7 and clearly indicate that there is a further hardening due to the thermal treatment, over and above that of the initial irradiation-induced hardening. A similar phenomenon has been observed by others, following elevated-temperature anneals, on the room-temperature tensile properties of molybdenum,⁵ niobium,⁶ and on mild and low alloy steels.⁷ Figure 4.8 compares the hardness values obtained by GE-NMPO (Figure 4.7) on irradiated molybdenum with the normalized room temperature yield strength measurements obtained by Wronski and Johnson.⁵ This apparent correlation between the hot-hardness and tensile test results indicates that hot-hardness measurements may be used to evaluate small quantities of alloy's prior to the testing of more expensive tensile and creep-rupture specimens. These screening studies can identify important temperature regions in which significant changes in flow properties may occur as a result of the degree of working and amount of irradiation, in addition to the determination of aging kinetics.

Fig. 4.7 - Room-temperature hardness of irradiated polycrystalline molybdenum as a function of temperature

⁵A. S. Wronski and A. A. Johnson, "A Hardening Effect Associated with Stage III Recovery in Neutron Irradiated Molybdenum," *Philosophical Magazine*, Vol. 8, 1963, pp. 1067-1070.

⁶M. J. Makin and F. J. Minter, "The Mechanical Properties of Irradiated Niobium," *Acta Met.*, Vol. 7, 1959, pp. 361-366.

⁷D. R. Harries, "Radiation Hardening in Mild and Low-Alloy Steels," *J. Iron and Steel*, Vol. 202, 1964, pp. 518-522.

Fig. 4.8 – Room-temperature yield stress and hardness of irradiated molybdenum as a function of the annealing homologous temperature

HIGH-TEMPERATURE ALLOYS

Status of Irradiations

Elevated-temperature capsule GEFP2-139 (previously⁸ designated GEFP2-128A) was irradiated for 2920 MwD during ETR cycle 70. This capsule, containing six Hastelloy N (INORD-8) and 12 special boron-containing A-286 alloy creep-rupture specimens, was scheduled for a full cycle at an irradiation temperature of 650°C. However, it was only irradiated at 650°C for approximately 1000 MwD in the first half of the reactor cycle. Prior to the mid-cycle shutdown, the ETR experienced a reactor scram. When the reactor was brought up to power, the specimen temperature remained at approximately that of the ambient water temperature. The capsule remained in the reactor position for the remainder of the cycle. After the scheduled reactor shutdown at the end of the cycle, the capsule was pressurized before removal from the reactor and found to have a large leak in the region of the small flange of the intake connector. The capsule was also pressurized with helium after removal from the reactor. No leaks were found in the assembly below the region of the flange known to have developed a leak. Visually, the condition of the capsule was good.

A careful survey of the lead tube and in-tank connector condition was made prior to, and following, the removal of the capsule. The following facts were established from this survey. The lower clamp above the capsule assembly was tightly gripping the lead tube. The upper clamp, positioned about a foot below the in-tank connector, was locked but not closed. With the clamp not closed, the lead tube was forced to move in the clamp in one degree of freedom through a total amplitude of 1.27 to 1.90 cm.

The direction of the freedom of motion of the tube in the clamp and the bending of the lead tube were so related to each other that the tube was relatively free to move in the clamp, and undoubtedly did so under excitation from the high turbulence of the water entering the upper part of the reactor from below the in-tank connector. The direction of the force on the weld that failed was almost perpendicular to the face of the flange, resulting in an unsatisfactory stress state.

⁸"High-Temperature Materials Program Progress Report No. 43, Part A," GE-NMPO, GEMP-43A, January 29, 1965, p. 56.

Corrective action with regard to the clamping problem has been taken for future capsule installations. The parts containing the failed weld will be examined following decontamination. A review is also being made of the weld joint design.

A third elevated-temperature capsule is being fabricated for the irradiation of Hastelloy N and A-286 specimens at 650°C. The capsule is scheduled for insertion in the next ETR cycle.

Hastelloy N Creep-Rupture Tests

A series of Hastelloy N creep-rupture specimens was tested at a temperature of 650°C. These specimens were irradiated in the ETR at reactor ambient temperatures for 1 cycle to a fast neutron dose of approximately 1×10^{20} nvt ($E_n \geq 1$ Mev).

Plots of the stress versus time to rupture are presented in Figure 4.9 for the specimens tested at 650°C. A comparison of control data at the lower temperature was also made with data obtained from specimens of the same heat as reported by ORNL.⁹ Based on these data, it appears that neutron irradiation of Hastelloy N to a fast neutron dose of 1×10^{20} nvt results in about a factor of 10 reduction in the time to rupture for these test conditions.

In addition to the reduction in the time to rupture, it has also been observed that, as in the other high-temperature alloys, severe embrittlement occurs in this material. This effect is shown in Figure 4.10 as strain versus time for a fixed stress at a temperature of 650°C. An expanded plot of the first 50 hours is shown in the inset.

Fig. 4.9 – Stress-rupture properties of Hastelloy N (INOR-8; Heat 5081) at 650°C

⁹"Molten-Salt Reactor Program, Semiannual Progress Report For Period Ending January 31, 1964," ORNL, ORNL-3626, July 1964, Figure 4.1, p. 62.

Fig. 4.10 – Strain versus time for Hastelloy N (INOR-8; Heat 5081) specimens tested in air at a temperature of 650°C and a stress of 24.6 kg/mm² (35,000 psi)

Annealing studies were initiated on this material. One specimen (see data in Figure 4.9) which was annealed for 100 hours at about 650°C and then tested at 650°C did not show any recovery. This effect is unlike that observed for the case of Hastelloy X, which did show recovery, although at a higher temperature, as a result of heat treatment.

Creep-rupture testing was initiated at a temperature of 815°C. Preliminary data indicate that the reduction in the time to rupture is not as great as that observed at the lower temperature.

WORK PLANNED FOR NEXT PERIOD

Post-irradiation creep-rupture studies of W, W - 25Re, and Mo specimens will continue with emphasis placed on annealing at the elevated temperatures with subsequent testing at the lower temperatures ($T < 0.31 T_m$).

Resistivity measurements of irradiated specimens will be performed at elevated temperatures for the case of tungsten irradiated to fast neutron doses of approximately 5×10^{19} nvt.

The refractory-metal tensile testing furnace temperature profile will be determined and the tensile measurements of irradiated tungsten will be resumed at the higher temperatures.

Hot-hardness testing of molybdenum in the warm-worked condition will be made and compared to the test results obtained for the case of irradiated molybdenum. Testing will be resumed on the tungsten single crystals which were irradiated at three different dosages. The influence of neutron dosage on the room-temperature and elevated-temperature hardness of tungsten will be evaluated and compared with the creep-rupture data.

Theoretical studies on neutron-induced defects in the BCC metals will continue. Substructure studies on tungsten creep-rupture specimens using the transmission electron microscope will be initiated.

Creep-rupture testing of irradiated Hastelloy N will continue at temperatures of 815°C. In addition, a series of control and irradiated specimens will be given a post-irradiation annealing heat treatment of 4 hours at a temperature of 870°C and will subsequently be tested at the lower temperature.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

5. HIGH-TEMPERATURE THERMOCOUPLE AND ELECTRIC MATERIALS RESEARCH

(57014)

The objective of this program is to identify and establish the properties of reliable high-temperature thermocouples and electrical and electronic materials to provide instrumentation and electrical components for long-life, high-temperature reactors and reactor experiments.

HIGH-TEMPERATURE THERMOCOUPLES

Thermoelement Development

Work was continued to develop thermocouples that would operate in a nuclear environment to 1800°C with adequate output and sensitivity and with negligible signal change over periods of time (1 to 2 years). Metals having low neutron cross sections and reasonably high melting points such as Mo, Nb, Ta, Ru, Os, Cr, Zr, and Ni are considered the most promising for preparing thermoelements having low transmutation characteristics.

The thermoelectric output characteristics of various metals and alloys tested versus W - 25Re¹ commercial wire are shown in Figure 5.1. As indicated in the figure, molybdenum and its alloys of Mo - 1Ru and Mo - 1 Os have the highest positive thermoelectric characteristics as a function of temperature when coupled with a W - 25Re thermoelement. The curves also show the thermoelectric difference between Mo commercial wire and a Mo rod sample made from commercial powders by methods previously described.² However, the thermoelectric difference is usually small and is attributable to minor variations in the impurity content. Similar differences can be observed between the Nb rod sample and Nb commercial wire. Analyses are being performed to identify impurity elements and their concentrations. To improve its thermoelectric characteristics, Nb was alloyed with Mo. The data shown for the Nb - 20Mo alloy indicate an improvement in the output of this alloy versus Nb rod. Metallographic inspection revealed, however, that all the Mo had not dissolved into the Nb in the Nb - 10Mo and the Nb - 20Mo alloy samples. Additional high-temperature homogenization treatments will be performed to obtain a complete solid solution in these two alloys. This may result in further improvement of the thermoelectric characteristics for these two alloy systems.

The alloys of Ru - 10Ni and Ni - 10Ru were thermoelectrically evaluated. The curves representing thermoelectric output as a function of temperature do not suggest any practical combinations of these materials with any of the materials studied. However, the Ru - 10Ni produced a fairly linear signal. The increasing positive slope of the thermoelectric output of tantalum, especially above 1000°C, makes its use undesirable with any of the other materials shown in the graph. Other materials such as zirconium and vanadium (not shown) were investigated and found to be too unstable for thermoelectric application.

¹Compositions in this section are in atomic percent except W - 25Re which is given in weight percent.

²"High-Temperature Materials Program Progress Report No. 27, Part B," GE-NMPO, GEMP-27B, September 30, 1963, pp. 69-70.

Fig. 5.1 - Comparison of thermoelectric output as a function of temperature for various metals and alloys versus W - 25Re commercial wire

The thermoelectric responses obtained from pure ruthenium and osmium³ are desirable materials with respect to the most positive materials, but as yet neither has been drawn into wire form.

Thermocouple Insulating Materials

Development of new materials for use as electrical insulators at high temperature and studies of available materials to determine their electrical insulating characteristics were continued.

The resistivities of ThO_2 and BeO were studied as a function of temperature and oxygen partial pressure. The two ThO_2 specimens measuring approximately 1-cm OD by 4-cm long were prepared by isostatically pressing the powders and sintering the compact. This technique has been previously described.⁴ A BeO specimen of the same size, having a purity of 99+ percent, was prepared at GE-NMPO by extruding, air-firing at 1500°F for 2 hours, and treating for 5 hours at 3000°F in hydrogen. This specimen was a sintered body having a fine grain structure and a density of 97 percent of theoretical. The techniques for measuring electrical resistivity were described previously.⁵ The electrical resistivity data are shown graphically in Figure 5.2. Generally, the resistivity of BeO is nearly two orders of magnitude higher than ThO_2 . This fact helps to explain why BeO has performed better in the past than ThO_2 as an electrical insulator in many of the high-temperature thermocouple circuits.

As indicated in the family of curves, the electrical resistivity of ThO_2 increases by an order of magnitude for every seven orders of magnitude that the oxygen partial pressure increases. As oxygen partial pressure increases, the number of oxygen vacancies in the lattice structure apparently decreases. Since an oxygen vacancy puts an electron into the conduction band of ThO_2 , a decreasing number of vacancies results in fewer electrons in the conduction band with a corresponding increase in resistivity.

The resistivity change of BeO with oxygen partial pressure was more complex. At high oxygen partial pressures and temperatures, the resistivity decreased sharply with increasing pressure, and permanent changes in the resistivity were observed at 1800°C as a result of prior heating to 2000°C . The resistivity at 1400°C increased with oxygen pressure. The factors controlling the resistivity changes in BeO are not understood, and further work is continuing at higher oxygen pressures to determine if the high-temperature behavior persists.

Magnesium oxide, a material having a melting point of approximately 2800°C , is known to have a high vapor pressure and to dissociate at temperatures far below its melting point reacting with materials such as rhenium and W - 25Re. In order to study the effect of loss of oxygen from the MgO , MgO was hermetically sealed in a W - 25Re capsule. The W - 25Re alloy was chosen because it has an extremely low permeability to oxygen. After heating the container of MgO for 3 hours at 2550°C in an argon atmosphere, the sample was bisected and examined metallographically for reaction zones. No reaction zones were found, and the crystalline MgO was still glass clear. The unsealed remaining half was returned to the furnace and again subjected to an identical thermal treatment. This time, however, the MgO dissociated and the magnesium reacted with the W - 25Re alloy. This test showed that, if oxygen is prevented from escaping, the oxygen partial pressure builds up within the closed system and prevents any dissociation of MgO . Further work is continuing to determine the factors controlling this unusual behavior. Possibly, this could lead to the development of a higher temperature electrical insulator.

³"High-Temperature Materials Program Progress Report No. 43, Part A," GE-NMPO, GEMP-43A, January 29, 1965, pp. 72-76.

⁴"High-Temperature Materials Program Progress Report No. 41, Part A," GE-NMPO, GEMP-41A, November 30, 1964, p. 73.

⁵"High-Temperature Materials Program Progress Report No. 39, Part A," GE-NMPO, GEMP-39A, September 30, 1964, pp. 35-37.

Fig. 5.2—Resistivity of ThO_2 and BeO as a function of temperature and oxygen partial pressure

HIGH-TEMPERATURE METAL-TO-CERAMIC SEALS

High-temperature gas-pressure-bonding techniques have been used successfully to fabricate ceramic-to-metal seals. Seals capable of withstanding at least 500 hours at 1600°C and rigorous thermal cycling to 1450°C were made⁶ between Nb and Lucalox⁷ alumina.

High-Temperature Graded Seals

Improved graded Nb-to-Lucalox seals were fabricated during this period. The improvement is the result of including the following five transitional zones of mixed Nb and Al_2O_3 powders between the Lucalox discs, 3.2 mm and 1.6 mm thick, and each of the Nb sheets, 0.5 mm thick.

1. 90 vol % Nb + 10 vol % (Linde A + 0.5 wt % MgO) (0.125 mm thick)
2. 70 vol % Nb + 30 vol % (Linde A + 0.5 wt % MgO) (0.125 mm thick)
3. 50 vol % Nb + 50 vol % (Linde A + 0.5 wt % MgO) (0.125 mm thick)
4. 30 vol % Nb + 70 vol % (Linde A + 0.5 wt % MgO) (0.125 mm thick)
5. 10 vol % Nb + 90 vol % (Linde A + 0.5 wt % MgO) (0.125 mm thick)

⁶"Fourth Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-334A, February 26, 1965, pp. 228–229.

⁷Trademark of the General Electric Company for commercial polycrystalline alumina.

A photomicrograph of one of the zones in this type of seal after bonding at 700 kg/cm^2 and 1650°C for 1 hour is shown in Figure 5.3.

Fig. 5.3—Photograph showing the microstructure of a Nb-to-Lucalox graded seal bonded at 700 kg/cm^2 , 1650°C , 1 hour. (Neg. 5707, as-polished, 100X)

A seal of this construction received 100 thermal cycles between 650°C and 1450°C at heating and cooling rates of 300°C per minute. The seal was still hermetic as indicated by a helium mass spectrometer test with a sensitivity of $10^{-10} \text{ cm}^3 \text{ (STP)/sec}$. Metallographic and crystallographic examination revealed no changes in microstructure due to the thermal cycling.

High Thermal-Conduction Bond - The bonding of Nb to BeO using gas-pressure-bonding techniques was investigated as a means of forming an electrically insulating bond of high thermal conductance. High thermal conductance is needed in certain electrical systems requiring a rapid flow of heat energy while preventing a passage of electric energy.

A thin sandwich of Nb and BeO was bonded at 700 kg/cm^2 and 1650°C for 1 hour. Two Nb sheets, 0.5 mm in thickness, encompassed a powder layer of BeO of 0.25 mm thickness and a diameter of 25 mm. Between the BeO layer and each Nb sheet, a 0.125 mm thick powder layer of Nb - 50BeO (vol %) was included to strengthen the bond. A photomicrograph of the bonded sandwich is shown in Figure 5.4. Excellent densification and bonding was achieved. The BeO layer had a varying grain size ($\sim 0.25 \text{ mm}$ maximum) with some grain boundary separation apparent. Further work in this system will include a grain growth inhibitor to strengthen the ceramic.

Fig. 5.4—Photograph showing the microstructure of a thin BeO layer between two Nb sheets, forming an electrically insulated but high thermal conductivity metal-to-ceramic seal
(Neg. 5606, as-polished, 100X)

WORK PLANNED FOR NEXT PERIOD

Thermocouple alloys in the Cr-Ru, Cr-Os, Mo-Ru, and Nb-Mo system will be thermoelectrically evaluated. The study of the electrical resistivity of the ceramic oxides of BeO, Y_2O_3 , and the rare earth oxides will be continued.

Continued studies will be performed on the development and test evaluation of graded Nb-to-Lucalox and Nb-to-BeO metal-to-ceramic seals for application to temperatures as high as 1600°C.

6. APPENDIX

The "High-Temperature Materials Program Progress Reports" previously issued in this series are listed below. The first two reports were each issued as one document, containing both the classified and unclassified portions. The subsequent reports were issued as two documents; part A, the unclassified portion and part B, the classified portion.

Report No.	Report Period	Publication Date
GEMP-1	May 1961 - June 30, 1961	July 15, 1961
GEMP-2	July 1, 1961 - July 31, 1961	August 15, 1961
GEMP-3, A and B	July 1, 1961 - August 31, 1961	September 15, 1961
GEMP-4, A and B	August 1, 1961 - September 30, 1961	October 15, 1961
GEMP-5, A and B	August 15, 1961 - October 15, 1961	November 15, 1961
GEMP-6, A and B	September 15, 1961 - November 15, 1961	December 15, 1961
GEMP-7, A and B	October 15, 1961 - December 15, 1961	January 15, 1962
GEMP-106, A and B		
(First Annual Report) Calendar Year 1961		February 28, 1962
GEMP-9, A and B	January 1, 1962 - February 15, 1962	March 30, 1962
GEMP-10, A and B	January 1, 1962 - March 15, 1962	April 16, 1962
GEMP-11, A and B	February 15, 1962 - April 15, 1962	May 15, 1962
GEMP-12, A and B	March 15, 1962 - May 15, 1962	June 15, 1962
GEMP-13, A and B	April 15, 1962 - June 15, 1962	July 31, 1962
GEMP-14, A and B	May 15, 1962 - July 15, 1962	August 15, 1962
GEMP-15, A and B	June 15, 1962 - August 15, 1962	September 14, 1962
GEMP-16, A and B	July 15, 1962 - September 15, 1962	October 15, 1962
GEMP-17, A and B	August 15, 1962 - October 15, 1962	November 15, 1962
GEMP-18, A and B	September 15, 1962 - November 15, 1962	December 14, 1962
GEMP-19, A and B	October 15, 1962 - December 15, 1962	January 25, 1963
GEMP-177, A and B		
(Second Annual Report) Calendar Year 1962		February 28, 1963
GEMP-21, A and B	January 1, 1963 - February 15, 1963	April 23, 1963
GEMP-22, A and B	January 1, 1963 - March 15, 1963	April 30, 1963
GEMP-23, A and B	February 15, 1963 - April 15, 1963	May 31, 1963
GEMP-24, A and B	March 15, 1963 - May 15, 1963	June 28, 1963
GEMP-25, A and B	April 15, 1963 - June 15, 1963	July 31, 1963
GEMP-26, A and B	May 15, 1963 - July 15, 1963	August 16, 1963
GEMP-27, A and B	June 15, 1963 - August 15, 1963	September 30, 1963
GEMP-28, A and B	July 15, 1963 - September 15, 1963	November 11, 1963
GEMP-29, A and B	August 15, 1963 - October 15, 1963	November 30, 1963
GEMP-30, A and B	September 15, 1963 - November 15, 1963	December 31, 1963

<u>Report No.</u>	<u>Report Period</u>	<u>Publication Date</u>
GEMP-31, A and B	October 15, 1963 - December 15, 1963	January 24, 1964
GEMP-270, A and B		
(Third Annual Report)	January 1, 1963 - January 31, 1964	February 28, 1964
GEMP-34, A and B	February 1, 1964 - March 15, 1964	April 15, 1964
GEMP-35, A and B	February 1, 1964 - April 15, 1964	May 28, 1964
GEMP-36, A and B	March 15, 1964 - May 15, 1964	June 19, 1964
GEMP-37, A and B	April 15, 1964 - June 15, 1964	July 31, 1964
GEMP-38, A and B	May 15, 1964 - July 15, 1964	August 19, 1964
GEMP-39, A and B	June 15, 1964 - August 15, 1964	September 30, 1964
GEMP-40, A and B	July 15, 1964 - September 15, 1964	October 15, 1964
GEMP-41, A and B	August 15, 1964 - October 15, 1964	November 30, 1964
GEMP-42, A and B	September 15, 1964 - November 15, 1964	December 18, 1964
GEMP-43, A and B	October 15, 1964 - December 15, 1964	January 29, 1965
GEMP-334, A and B		
(Fourth Annual Report)	January 1, 1964 - January 31, 1965	February 26, 1965
GEMP-46, A and B	February 1, 1965 - March 15, 1965	April 15, 1965

ADVANCED TECHNOLOGY SERVICES
GENERAL ELECTRIC